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HEAVY METAL CONCENTRATIONS IN SEDIMENTS FROM ACCRETING AND ERODING REGIONS ALONG THE COAST OF GUYANA

By

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ABSTRACT

This thesis examined heavy metal concentrations of sediments from accreting and eroding beaches along the coast of Guyana to determine if differences occurred between the two beach types as well as within both beach types. A total of 24 samples were taken from two separate beaches and were subjected to dry sieving analysis. From the results of the dry sieving procedures, it was determined that that only those sediments less than 4 phi in diameter would be subjected to heavy metal analysis. A total of 96 samples were submitted to the Great Lakes Institute for Environmental Research (GLIER) for chemical analysis. Twenty-four of the samples were bulk samples less than 4 phi in diameter. Seventy-two of the samples consisted of sediments from each of the grain-size fractions that comprised the restrictive grain-size fraction (4,5 and > 5 phi fractions).

Discriminant analysis and analysis of variance were conducted to determine if accreting beaches, with smaller grain-sizes and eroding beaches, with larger grain-sizes exhibit contrasting concentrations of heavy metals. Two separate series of line graphs were constructed to ascertain whether spatial variations in the concentrations of heavy metals were discernible and distinct in both across-shore and along-shore directions within accreting and eroding beaches. Lastly, correlation and regression analysis was performed to reveal the role of grain-size in the spatial distribution of heavy metals.

The results of discriminant analysis and analysis of variance revealed that variations in the concentrations of heavy metals between accreting and eroding beaches exist. From the two series of line graphs, it was determined that discernible and distinct spatial variations in the concentrations of heavy metals exist in both along-shore and across-shore directions. Grain-size was discovered to have had a pronounced effect on the spatial distribution of heavy metals. Lastly, questions surrounding the effectiveness of restrictive grain-size fractions in reducing the effects of grain-size bias were raised.

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CHAPTER 1

1.1 Introduction

Marine environment contamination by trace metals has received increased global attention during recent years. Presently, it is widely recognized that marine ecosystems can become contaminated by trace metals from numerous and diverse sources. However, anthropogenic activities, such as mining and industrial processing of ores and metals, still remain the principal cause of the increased amount of heavy metals which are released into oceans (Pardo *et al.*, 1990). After entering the aquatic environment, heavy metals are usually absorbed onto particle surfaces and are removed as the particles settle to the bottom (Daskalakis and O'Connor, 1995). There they provide a resevoir of contaminants that can be released to the overlaying waters through natural or anthropogenic processes. The magnitude of this action depends on the physical, chemical and biological properties of the sediment.

Investigations that have sought to account for the spatial distribution of heavy metals in beach environments have focused primarily on their location in relation to point sources of pollution as well as their distribution in along-shore and across-shore directions. Several investigators have implicated particle size as the predominant factor controlling the spatial distribution of heavy metals. While numerous investigations pertaining to the spatial distribution of heavy metals have been conducted and the relationship between particle size and heavy metal concentrations has long been known, few investigations have related heavy metal concentrations to beach state.

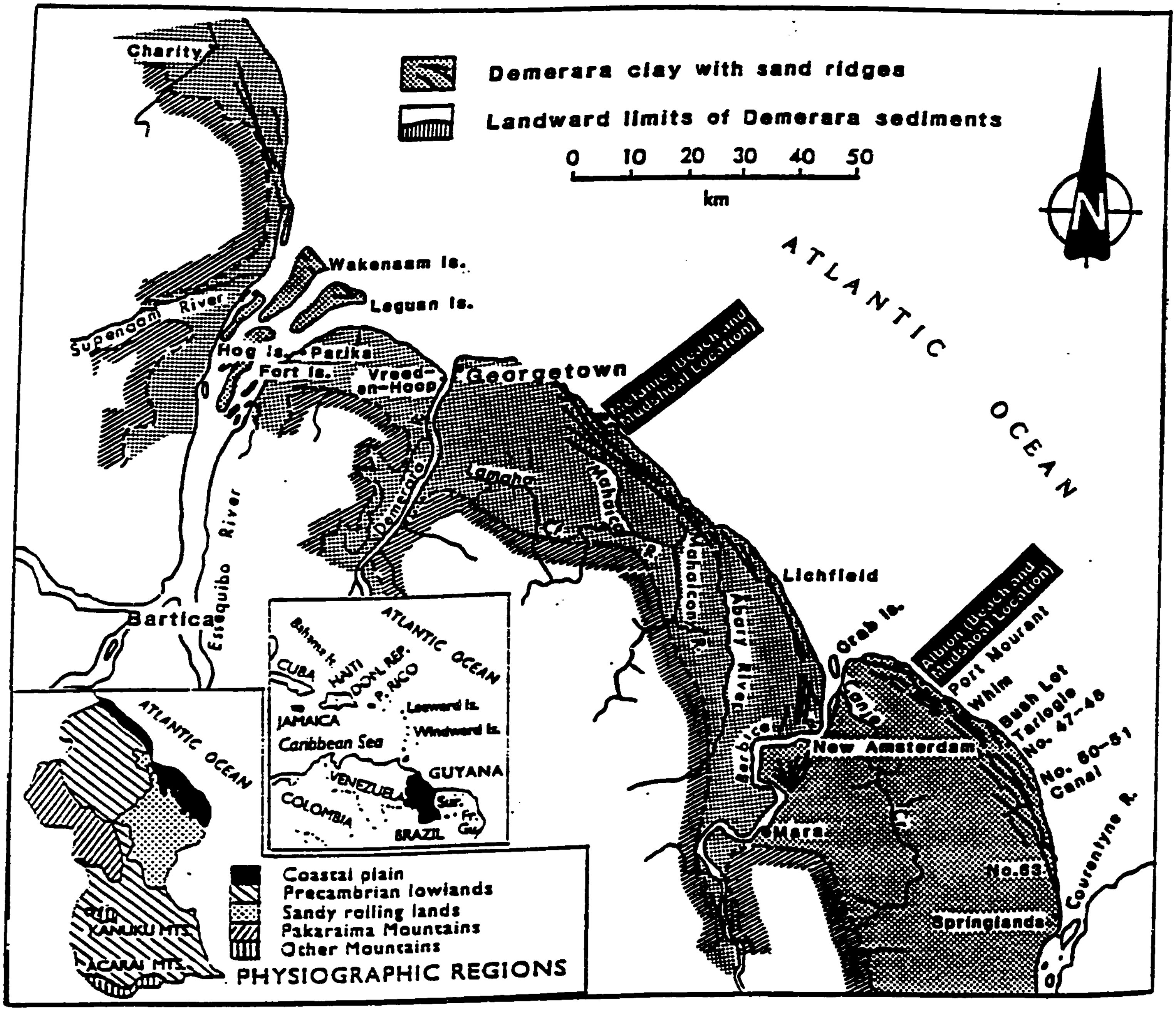
Since there exists a paucity of research pertaining to the relationship between heavy metal concentrations and beach state, this investigation will compare the concentrations of heavy metals in surficial sediment samples of separate and distinct accreting and eroding regions of the coast of Guyana. The Guyana coast represents an ideal region for studying the relationship between heavy metal concentrations and beach state as it displays distinct zones of accretion and erosion. These distinct zones are the direct result of migrating mudshoals, which mark the coast (Lakhan and Pepper, 1997). As well as having distinct regions of accretion and erosion, the majority of heavy metals present within the region have been identified as originating from a single source, the Amazon river (Eisma and van der Marel, 1985).

An examination of the spatial distribution of heavy metal concentrations in surficial sediments in separate and distinct regions of the Guyana coast will also be conducted. This examination serves to further previous work conducted by the author along the coast of Guyana (Cabana, 1997). More specifically, theories pertaining to the spatial distribution of the grain-size of sediment along the Guyana coast will be used to formulate new hypotheses pertaining to the spatial distribution of heavy metals in surficial sediments along the coast of Guyana.

1.2 Region Under Study

The area under study is the near-shore zone of Guyana. Guyana is located on the northern coast of South America, between 0° 41' N and 8° 33' N and between 56° 32' W and 61° 22' W (Bowes, 1991). Suriname bounds the country of Guyana to the east, Venezuela to the west, Brazil to the south, and the Atlantic Ocean to the north. With a width of between 77 km in the west, and 26 km in the east, the coastal zone is the country's smallest physiographic region, occupying less than 5% of Guyana's surface area (Figure 1.1). Despite being the smallest physiographic region within the country, the

Figure 1.1: The Coastal Zone of Guyana



Source: Lakhan (1994b)

coastal plain houses 90% of the country's population. The coastal plain is currently utilized for agriculture, roadways, urban centres, and tourism.

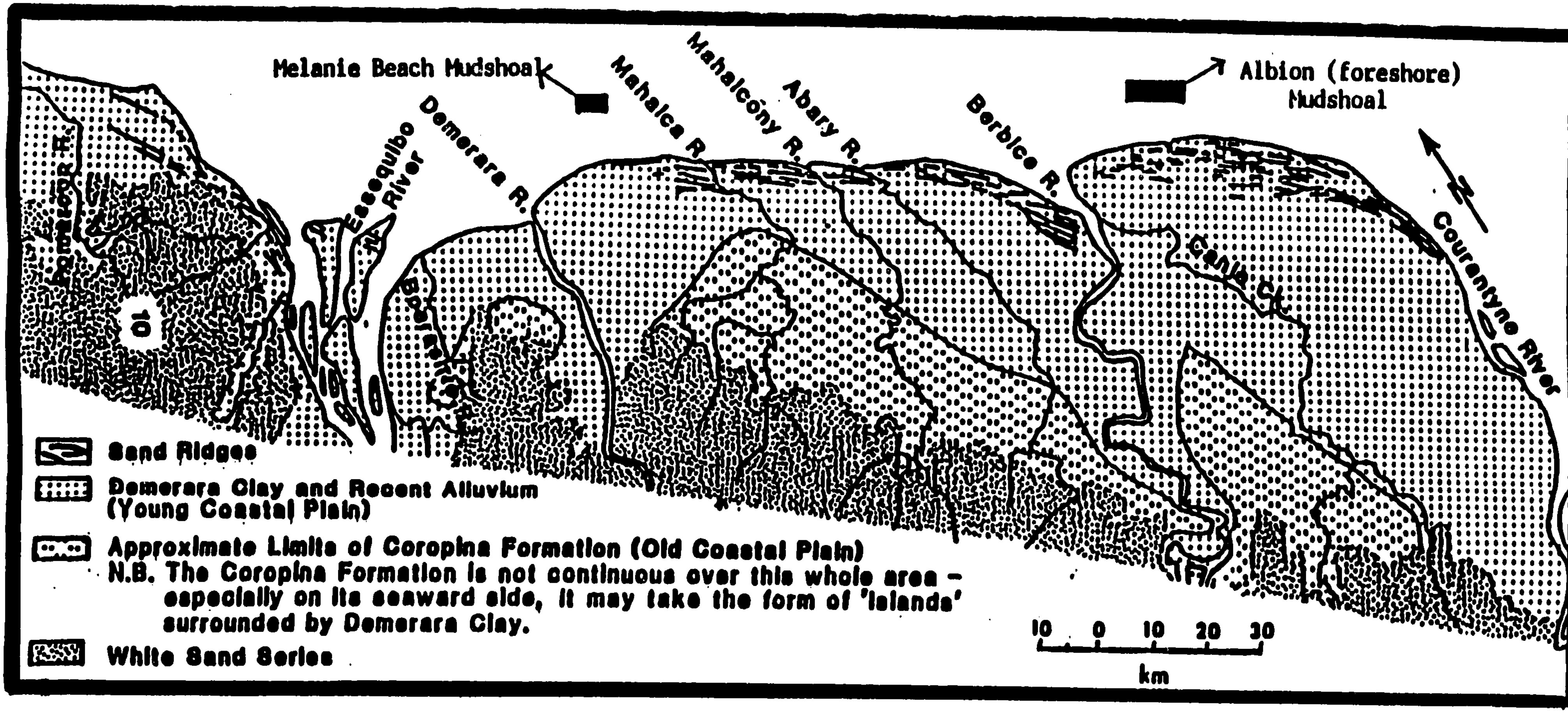
1.2.1 Generalized Geomorphology of Coastal Guyana:

Figure 1.2 illustrates the generalized geomorphology of coastal Guyana. The shoreline is noticeably flat. Very gentle slopes of 1:3000 or less are common. The coast is intersected by the mouths of a number of fairly large rivers including the Courantyne, Berbice, Demerara, and the Essequibo which debouch perpendicularly to the coast. Several smaller rivers also intersect the coast and show a tendency to bend to the west before reaching the coast or the mouth of a larger sister river.

The configuration of the coastline is primarily determined by large, migrating, aqueous bodies of mud, called mudshoals. The presence or absence of mudshoals, influences whether the coast is accreting or eroding (Augustinus, 1987). Accretion takes place on the coast directly opposite the mudshoal, while erosion occurs along the coast opposite to troughs situated between two adjacent mudshoals. The mudshoals occur in a zone, landward of the 18 m isobath, extending approximately 20-25 km from the shoreline. They very in length from only a few kilometres up to 45 km, and their migrating velocities are on average 1.5 km per annum which leads to an average period of recurrence of 30 years (Allersma, 1971). The average wavelength is about 45 km with variations between 30 and 60 km.

Regional surface sediment distribution of the Guyana coast differs from "typical" coastal sediment distributions. According to Reineck and Singh (1975), the typical coastal system is a transition from nearshore sand to offshore mud. The Guyana coast, which is termed a muddy coast based on the classification of McCave (1972), has an inverse

Figure 1.2: The Generalized Geomorphology of Coastal Guyana



Source: Lakhan (1994b)

distribution with the majority of nearshore sediments being clays to silty clays with less than a 5% sand component (NEDECO, 1962). Seaward of this band of mud is a very sandy surface of mixed sand, shell, and mud (Nota, 1958).

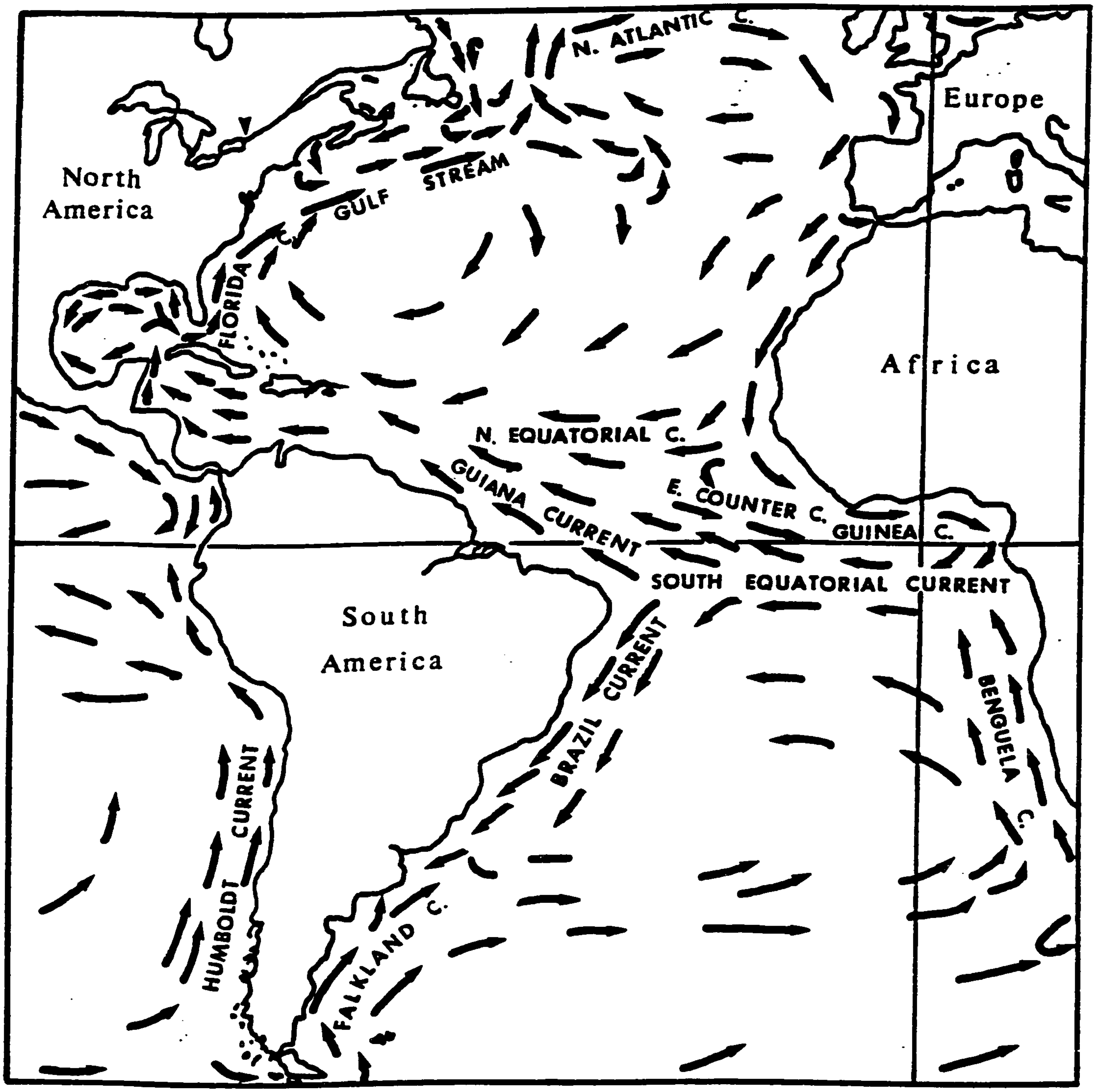
While it is true that the Guyana coast is a muddy coast, and that atypical sediment distributions typify the coast, Cabana (1997) has demonstrated that pockets of normal near-shore sediment distributions exist. The atypical sediment distributions described by the above investigators epitomise accreting beaches, stable beaches or those that are in the early stages of erosion. Coastal regions that have been subjected to a consistent and lengthy period of high energy input tend to exhibit more normal near-shore sediment distributions.

1.2.2 Sediment Transport Along the Guyana Coast:

Few investigations pertaining to the transport of heavy metals along the coast of Guyana have been conducted. However, it is suspected that heavy metals are transported in the water column in a dissolved phase, as well as in a particulate phase (attached to sediments). Since heavy metals are known to travel in both a dissolved phase and a particulate phase along the coast, insight into the transport of sediment along the coast is essential.

The majority of sediments along the Guyana coast originate from the Amazon river, which is located some 400 km from the study area, a fact that was inferred by Lyell (1832) and confirmed by Eisma and van der Marel (1971). In addition, lesser amounts of sediment are supplied by smaller rivers. Even smaller amounts are derived locally. These sediments are those which have been eroded from the coast. According to Rine and

Figure 1.3: Major Oceanic Currents Affecting Northern South America



Source: Lakhan (in Press)

Ginsburg (1985), the muddy coast of Guyana is in effect an attenuated delta of the Amazon River.

Three major currents are responsible for sediment transport along the coast of Guyana (Vann, 1959) (Figure 1.3). The Guiana Current, flows in a north-west direction and affects waters 37-185 km offshore. This current has velocities of 1.9-5.6 km per hour. The Guiana Current does not directly affect sediment transport, but does carry sediment in suspension which are in turn carried to the shore by tidal currents and waves (Vann, 1959). Augustinus (1987) has estimated that this current transports between 0.25 and 0.9 x 10^{10} tonnes of sediment per annum.

The majority of sediment transport along the coast results from wave generated long-shore currents. The wave generated long-shore currents are highly seasonal. These currents have their greatest effect during the short rainy season (December to February). Winds that produce these currents, generally blow from directions between north-east and south-east and slightly stronger along the eastern part of the coast. The greater speeds, with averages of 6 to 8 m per second, occur in the spring mainly from between north-east and east, while lower speeds of 3 to 4 m per second are observed from July to November mainly from the east. Waves and swell follow the same pattern with heights of approximately 2 m from December to June and 1 to 1.5 m from July to November. The origin of the waves and swell varies slightly between north-east and east. The average period of the waves is about 6 seconds, but periods of up to 13 seconds have been observed (NEDECO, 1962).

An additional current affecting sediment transport along the coast is the tidal current. This current affects the coast year round. During flood tides, a steep velocity gradient is formed generating currents that flow in an on-shore direction. This current carries sediment shoreward and deposits large volumes of sediment along the shoreline. Two high and low tides occur daily. The average tidal period is approximately 13 hours. The mean tide is 1.3 m above the mean low water spring levels (Vann, 1959). Because of the vast width of the coastal shelf, and the gentle slopes found along the Guyana coast, tidal ranges along the coast are larger than normal.

1.2.3 Study Area:

Several areas of accretion and erosion exist along the coast of Guyana. However, this investigation focused on one region of accretion and one region of erosion only. Accretion along the coast primarily occurs landward of the migrating mudshoals. The zone of accretion from which samples were extracted in this study lies directly behind the Albion mudshoal (Figure 1.2). The Albion mudshoal has an approximate length of 10 km. Sampling was conducted in front of the districts of Plantations Albion and Port Mourant which corresponds roughly with the middle of the region of accretion. The Melanie beach mudshoal is currently dissipating at its western most margin. As a result of its dissipation, the shoreline has become exposed and is currently being eroded. Samples were also extracted from Melanie beach, which is located in front of the districts of Melanie and Stratspey (Figure 1.2).

CHAPTER 2

2.1 Review of the Literature:

Following an exhaustive search for investigations pertaining to the relationship between heavy metal concentrations and beach state it has been determined that investigations of this nature have not been conducted. Researchers have, however, conducted investigations pertaining to the cycling of heavy metals in coastal environments. Investigations of this nature provide the necessary background for understanding the primary mechanisms involved in the distribution of heavy metals.

Shrestha and Orlob (1996) have identified the interrelationships of some key processes determining the fate of cohesive sediments and associated heavy metals in estuarine environments. According to these investigators, sediments in suspension are advected and dispersed through the bounding aqueous surfaces and exchanged at the water column-sediment bed interface by deposition and scour. Heavy metals are partitioned between aqueous and solid surfaces of the water column and the bed, depending on the properties of the metal species and sorbent and environmental factors such as pH, temperature, and salinity. According to Shrestha and Orlob (1996), dissolved metals may be diffused between the water column and pore water in the bed, and when sorbed on particle surfaces may be deposited with discrete particles or as flocs, later to be returned to the water column by erosion.

Shrestha and Orlob (1996) have indicated that a key process influencing the distribution of sediments and toxin concentrations within the water column is the aggregation of suspended sediment particles, resulting in enlarged flocs that settle more rapidly to the bed carrying with them associated toxins. Aggregate size and density depends on shear rates prevailing in the flow; lower shear rates allowing the formation of higher order (more rapidly setting) aggregates. According to Shrestha and Orlob (1996), as aggregates settle, shear stresses nearest the bed level determine whether the aggregates can actually reach the bed, or instead may be broken up and resuspended into the water column because their shear strengths are less than the induced stresses.

Shrestha and Orlob (1996) have indicated that depending on the shear stress in the fluid near the bed and a critical shear stress that allows deposition to occur, sediment is deposited onto the bed. During a period of deposition, i.e., when near bed stress is less than critical, a layer of sediment is added to the bed. According to Shrestha and Orlob, if no intervening scour occurs, another layer may be formed, thus building the bed in a succession of layers, each with specific properties identified with the sediment deposited, e.g., thickness, shear strength, toxicant/sediment mass ratio etc. On the other hand, if shear stresses at the bed level are greater than the shear strength of the uppermost sediment layer, erosion occurs and sediment and related toxicants are resuspended, exposing the new bed surface to either subsequent erosion or deposition.

Despite a paucity in the research concerning the relationship between heavy metal concentrations and accreting and eroding coastal regions, it is believed that sufficient information can be gained from indirect investigations. An assessment of investigations pertaining to the grain-size characteristics of sediments in accreting and eroding regions of coasts as well as the relationship between heavy metal concentrations and the grain-size of sediments should provide the necessary information from which an adequate understanding of the study problems can be gained. This literature review will, therefore, be conducted in two parts. First, an examination of research pertaining to the relationship between the grain-size of sediment and beach state will be conducted. Following, a review of the research that has focused on the relationship between heavy metal concentrations and the grain-size of sediments will be performed.

2.1.1 Grain-Size Characteristics of Accreting and Eroding Shorelines:

The relationship between the grain-size of sediments and beach accretion and erosion in coastal regions has been extensively investigated. Such investigations are well documented throughout history. For instance, Hjulstrom (1939) plotted the critical tractive velocity at which grain movement begins against grain-size. Hjulstrom indicated that for coarser grains, the size of the material moved is proportional to wave velocity. He further noted that in finer sediments, due to cohesive forces, this relationship breaks and the energy needed for setting grains in motion increases with decreasing grain-size. Hjulstrom's work set the stage for future research on erosion and accretion in coastal environments.

For instance, Folk and Ward (1957) discovered that graphic statistical parameters are sensitive to the energy differences and the patterns of transport and accumulation in advancing and receding beaches. In particular, when comparing mean size, kurtosis, skewness, standard deviation, and percentage of pelite ($> 4\phi$), diagrams were obtained in which the field of accreting beaches was sufficiently separated from eroding beaches. With respect to this separation, Folk and Ward concluded that finer sediments are found in lower energy environments and coarser sediments in higher energy environments. Similar results have been revealed by, among others, Miller and Zeilgler (1958), Ingle (1966), Klovan (1966), Friedman (1967), Martins (1967), Visher (1969), Curray (1969), King (1972) and Hails (1974).

Dal Cin (1975) also sought to determine the relationship between the grain-size of sediments and beach erosion and accretion in a coastal environment. This investigation continued previous research conducted by Dal Cin (1968, 1969). Dal Cin's research was based on that of Folk and Ward (1957). It was Dal Cin's contention that a more accurate statistical treatment and objective correlation of the numerous grain-size data could be obtained with the use of a multivariate statistical technique such as Q-mode factor analysis. Dal Cin conducted factor analysis on 179 samples collected along beaches with accreting and eroding tendencies in Italy. According to Dal Cin, four factors accounted for the initial information. These primarily represented the following: fine and very fine sands, medium-fine sands, medium-coarse sands, and the fractions lying between 2.25ϕ and 2.50ϕ.

By making various comparisons among the four factors, diagrams, which adequately distinguished advancing beaches from receding beaches, were obtained. The results indicated that advancing beaches are particularly rich in very fine and medium-fine sands while receding beaches are richer in medium-coarse. Dal Cin hypothesized that the principal cause of the variations in the factors obtained is the differing energy levels and the varying sediment supply on the two types of beaches. In addition, the grain-size of the available material was thought to be an important factor.

Several more recent investigations pertaining to the relationship between grain-size and beach state have also been conducted. Two of these investigations are discussed here. An overall estimate of the relationship between the changes in near-shore morphology, the evolution of the sedimentary budget, the beach morphodynamics, and the variation of grain-size characteristics along the beach of Thau Lagoon in France were made by

Barusseau *et al.* (1994). Barusseau *et al.* synthesized data from different surveys which included: a basic survey of two separate grids of 11 closely-spaced transverse profiles during 1989-1991, an along-shore baseline survey of 11 beach profiles (1988-1991), and an earlier survey of 6 widely spaced bathymetric profiles covering discretely the whole stretch of the near-shore zone.

Sediment sampling locations were determined based upon the surveys. The collected sediments were examined with emphasis on grain-size analysis and the textural characteristics of the different types of sand were determined. From their analysis of the grain-size of the sediment samples, the investigators determined that the spatial variation of grain-size characteristics was large. The long-shore differentiation in mean diameter and in sorting and skewness parameters was discovered to be consistent with the evolution of the accumulation-erosion processes. That is smaller mean values were present in accreting regions while larger mean values were located in eroding regions.

In a similar investigation conducted by Guillen and Jiminez (1994), the long-shore variation of sediment grain-size on the Ebro Delta coast was investigated to estimate which processes control its distribution. Thirty control points along the coast were used. From these control points a representative sample was obtained by averaging four samples taken in the inner part of the surf zone during eight field campaigns. The obtained distribution was related to the long-shore variation of a set of parameters characterizing beach processes, which included: shoreline evolution trends, net long-shore sediment transport, and near-shore wave power. The investigators discovered that the sediment grain-size distribution along the Ebro Delta coast shows a non-monotonic long-shore sorting process of sediment related to the long-shore variations of the main driving agents (long-shore transport and wave power). Guillen and Jiminez inferred that finer sediments are characteristic of areas of deposition, with lower power and negative long-shore transport gradients while coarser sediments are present in eroding zones associated with high wave power and positive long-shore transport gradients.

In addition to the above, many researchers have conducted investigations pertaining to the spatial analysis of shoreline accretion and erosion, shoreline classification, beach stability and the cyclic characteristics of beach sediment. While these investigations do not focus directly on the relationship between grain-size and eroding and accreting shorelines, one could infer from each investigation that smaller grains are associated with accreting regions while larger grains are associated with eroding regions. Among these investigations are those conducted by Zenkovich (1945), Yasso (1971), Sonu (1972), Miller (1973), Gleason *et al.* (1975), Phillips (1986), Hanamgond and Chavadi (1992), Dal Cin and Simeoni (1994), and Douglas (1994).

2.1.2 Grain-Size and Heavy Metal Concentrations:

Several investigators have conducted research on heavy metal concentrations. A review of these investigations reveals that the spatial distribution of heavy metal concentrations is most often the focus. Several investigators have sought to relate the spatial distribution of heavy metal concentrations to numerous physical and chemical characteristics. The grain-size of sediment has received particular attention. A review of the recent, pertinent literature reveals that in coastal and marine sediments, there is usually a dependence of heavy metals on grain-size. Due to the voluminous amount of literature that exists, and the similarity of results among the research, not all investigations will be reviewed.

Sakai *et al.* (1984) have examined the distribution of manganese, zinc, copper, lead, chromium, and cadmium in water and sieved sediment samples taken from the main stream of the Toyohira River. Water and sediment samples were collected from 13 sites along the river. The samples were passed through a vertical nylon nest of five sieves with openings ranging from 4ϕ to -1.7ϕ. The particle sizes were ranked A (largest) to D (smallest), but fraction AA ($>- 1.7\phi$) was excepted in the study because it contained a variety of twigs and pebbles. Conventional atomic absorption methods using a Hitachi 707 Zeeman Flameless Atomic Absorption Spectrophotometer were performed to determine the heavy metal concentrations of the samples. Sakai *et al.* discovered that heavy metal concentrations were dramatically different between fractions A and D. The investigators noted that heavy metal concentrations generally increased with decreasing particle size.

In a similar investigation, Wayne and Waters (1988) examined bottom sediment textures and heavy metal contamination in U.S. Gulf coast bays and estuaries. According to Wayne and Waters, bottom sediment textural characteristics of northern Gulf of Mexico bays and estuaries are distinctive for each and clearly reflect the sediment source, rocks, and weathering regiment within the watersheds. Both Pensacola Bay and Mississippi Sound acquire all of their sediments from younger coastal plain formations and as a consequence, are dominated by silt and sand-sized material. Mobile Bay, in contrast, possesses a significantly larger clay component because the rivers that contribute sediment to the bay originate far to north with the Ridge and Valley Cumberland Plateau and Piedmont physiographic provinces. The sediments of Apalachicola Bay, Florida are similar in this respect but, unlike Mobile Bay sediments, are markedly deficient in silt-sized components. This is because the construction of numerous dams on the rivers that empty into this bay have acted to trap most of the silt causing the incoming sediment load to be dominated by clays and sands.

According to Wayne and Waters (1988), the textural composition of these bays is important in that the size of the particulate matter exerts important controls upon the "pollution potential" of each bay. The reason for this stems from the fact that heavy metal contaminants are most easily concentrated in sediments that are smaller in diameter. Because of this, the investigators were not surprised that Mobile Bay was found to possess the highest level of heavy metal contamination of any bay in the northern Gulf of Mexico. Pensacola Bay and Apalachicola Bay, having higher sand contents, showed significantly lower levels of all heavy metal species.

Biksham *et al.* (1991) examined the distribution of heavy metals in the Godavari River Basin in India. Biksham *et al.* sought to account for the spatial variations of heavy metal concentrations in this region. Suspended and bed sediments were collected for the entire study region and were analyzed in terms of several physical and chemical properties. The grain-size of the sediments in which the heavy metals were located was examined. Size fractions of the bed sediments were separated by standard sieving methods. The bed and suspended sediments were analyzed for silicon and aluminum by the solution techniques suggested by Shapiro and Burnock (1962). The rest of the major and minor elements were analyzed by a thin-film X-ray fluorescence technique (XRF). The results of their investigation revealed that, in general, concentrations of heavy metals in the suspended sediments are higher than the bed sediments in the basin. The investigators further revealed that grain-size significantly affects the metal distribution of sediments in the Godavari River. According to Biksham *et al.*, there is a general increase of heavy metal concentrations in the finer fractions (>5.6ϕ), which is 40 percent more compared to the coarse silt and fine sand fraction. It is Biksham *et al.*'s opinion that higher concentrations of heavy metals in the finer fractions are due to the increase in the specific surface area of these sediments.

A similar study was conducted by Arakel and Hongjun (1992). In their investigation, Arakel and Hongjun examined heavy metal geochemistry and dispersion patterns in coastal sediments, soil, and water of the Kedron Brook floodplain area in Brisbane, Australia. These investigators subjected 32 randomly sampled, thirty gram surface samples of sediment to grain-size analysis in order to assess the relationship between heavy metal content and grain-size. A combination of dry-wet sieving and pipette analysis was performed to establish sand (> 3.0ϕ), course silt (> 4.0ϕ), fine silt (> 7.6ϕ), and clay (> 7.6ϕ) grain-size categories. The metal concentrations were determined by Atomic Absorption Spectrophotometry (AAS) with a graphite furnace attachment. The results of their investigation revealed that greater concentrations of heavy metals were located in the clay grain-size category. More moderate concentrations of heavy metals were discovered in the fine silt and course silt grain-size categories. Sands had the lowest concentrations of heavy metals.

In addition to the above investigations, research conducted by Abernathy *et al.* (1984), Thompson *et al.* (1984), Ergin (1991), Modak *et al.* (1992), Van Hattum *et al.* (1993), Chakrapani and Subramanian (1993), Maurer *et al.* (1994) and De Gregori *et al.* (1996) have revealed similar findings. Findings that indicate heavy metal concentrations increase with decreasing particle size. A consensus among investigations revealed that this relationship is primarily the result of higher surface area-to-grain-size ratios which are characteristic of sediments smaller in size.

The above investigations clearly show that the extent of heavy metal enrichment is greatest in smaller sized grains. In fact, the relationship is so pronounced and widely accepted that many investigators have attempted to circumvent the effects of grain-size bias in heavy metal concentrations. Mantei and Coonrod (1989) used the $<3.4\phi$ to $>3.8\phi$ (fine sand) size. The $>3.8\phi$ to 4ϕ (very fine sand) size fraction was used by Mantei and Foster (1991). Some studies have used less restrictive grain-size fractions. Compest (1991) discovered that trace metal trends in sediments downstream from an emission source may not be recognized in the $<-1\phi$ sediment size fraction. Salomons and Forstner (1984) and Rule (1986) concluded that the $> 4.0\phi$ (clay/silt) size sediment fraction contains the greatest concentrations of heavy metals. Similar investigations conducted by Fatimad *et al.* (1988), Ntekim *et al.* (1993), and Axtmann *et al.* (1997) also came to this conclusion. Singh *et al.* (1996), however, used the $>7.6\phi$ grain-size fraction to minimize the grain-size dependencies of heavy metals.

While numerous investigators have used restrictive fine grain sediment fractions, White and Tittlebaum (1985) have indicated that their use does not adequately reduce bias among samples. According to White and Tittlebaum, data has shown that sediment sizes of greater than 8.8ϕ are capable of absorbing three times more metal than a sediment size between 7.6ϕ and 4ϕ. These investigators advocate the use of relative atomic variation (RAV), as proposed by Allan and Brunskill (1976), to reduce grain-size effects on heavy metal accumulations in sediments. In theory, the relative atomic variation is an independent geochemical index correlating one metal to another. This dimensionless index is the numerically expressed slope of the significant linear regression line for a particular metal pair. The initial step in determining the RAV is to construct a plot of "metal A" concentrations versus "metal B" concentrations. The RAV is the numerical value of the slope of the best-fitting straight line through these plotted points. Linear regression techniques are used to determine the best fitting line. Thus in actuality, the RAV can be thought of as the average ratio of one element to another. According to White and Tittlebaum, similarity in the RAV implies a similarity in the geochemical cycle in a large number of factors including grain-size. This method has also been utilized by Ergin (1991), and Murray (1996).

While several investigators have used restrictive fine grain-size sediment fractions and the RAV method as a way of reducing the effects of grain-size bias, other investigators have used normalization methods to accomplish this task. Normalization is most often used in investigations seeking to discover the intensity of pollution by heavy metals in a given environment. Normalization procedures involve comparing heavy metal concentrations as ratios to another constituent of the sediment.

The chosen constituent is one that is most often associated with finer particles. Constituents are most often other heavy metals. For instance, aluminum is most commonly used because it can serve as a measure of the clay content of a sediment sample. Aluminum is a major constituent of clay minerals. Aluminum as a normalizing parameter, has been utilized by several investigators including, among others, Kemp *et al.* (1976), Ryan and Windom (1988), Windom *et al.* (1989) and Daskalakis and O'Connor (1995). Iron has also been used as a normalizing parameter (Sinex and Wright, 1988; Helz and Valletta, 1992; and Morse *et al.*, 1993). A variety of other metals have also been used to a lesser extent including Rubidium and Lithium. Total organic carbon (TOC) has also been used as a normalizing parameter.

2.2 *A priori* Model:

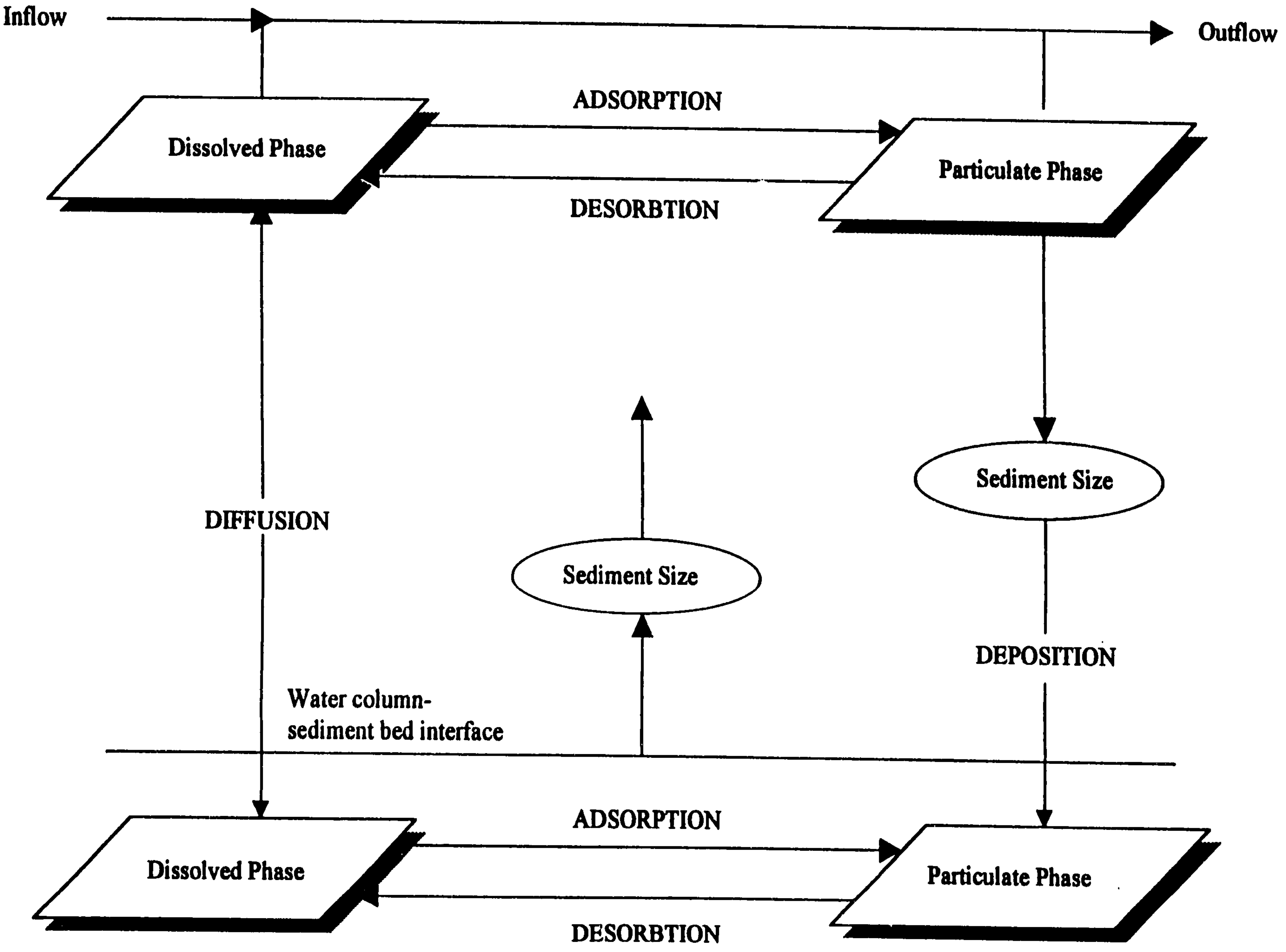
A review of the literature has revealed that a relationship between the grain-size of sediment and beach state exists such that advancing beaches have a higher percentage of finer grains while receding beaches have a higher percentage of coarser grains. This relationship is directly attributable to the onshore wave component (Murray, 1996). The literature review has also revealed that the spatial distribution of heavy metals is dependent upon the grain-size of sediment. In most instances, an inverse relationship exists between the concentration of heavy metals and the grain-size of sediments. Higher concentrations of heavy metals generally accumulate in smaller sediment grain fractions because of the higher surface area-to-grain-size ratio (Mantie and Sappington, 1994).

The two relationships outlined above as well as the theory utilized by investigators to explain them have revealed much about the nature of the spatial distribution of heavy metal concentrations in near-shore coastal environments. Based on these two relationships as well as the theory utilized by investigators to explain them, an a priori model was conceptualized (Figure 2.1) and the following hypothesis is advanced:

> Accreting beaches, with smaller grain-sizes and eroding beaches, with coarser grain-sizes exhibit contrasting concentrations of heavy metals.

Figure 2.1 is based on the previous work of Shrestha and Orlob (1996). In its original form, this model was utlized to describe the fate of heavy metals in a dynamic estuarine environment. Mass fluxes of heavy metals on the coast, as a result of deposition and erosion by scour, are predicted by the model. Estuarine environments are typically

Figure 2.1: A *priori* Model



Source: Adapted and Modified from

Shrestha and Orlob (1996)

mud dominated. While it is recognized that the Guyana coast is a mud dominated environment, the model conceptualized by Shrestha and Orlob does not account for variations in the grain-size of sediments. For the purpose of this investigation, the variable grain-size has been incorporated into the Shrestha and Orlob model.

The model is described in terms of various inputs, outputs, states, and processes. Inputs include energy, sediment, and heavy metals. Offshore currents, the long-shore current, and tidal currents comprise the bulk of the energy inputs. The majority of sediment and heavy metal inputs have their origin in the Amazon river. Additional sediment and heavy metals are supplied from numerous smaller rivers that mark the coast. As well, a smaller portion of sediment are derived locally via erosion of the coast. The outputs of the system also include energy, sediment, and heavy metals.

The model demonstrates that heavy metals exist either in a dissolved or a particulate phase/state. The variable sediment size is the only variable to have been included in the model. The processes of erosion and deposition of sediment are both dependent upon the grain-size of sediments in the water column and bed respectively. Generally, larger sediments are the first to be deposited while smaller sediments are the first to be eroded.

The model contains six predominant processes which include: 1) advection and dispersion of suspended sediments; 2) advection and dispersion of heavy metals; 3) absorption and desorption of dissolved toxicants to and from sediment surfaces; 4) deposition of sediment and thus heavy metals; 5) erosion of particles and heavy metals from the sediment bed; and 6) heavy metal source/sink terms due to erosion/deposition of sediment.

A second hypothesis, based on the premises pertaining to the relationship between heavy metal concentrations and the grain-size of sediment, and previous findings from work conducted by the author (Cabana, 1997) on the spatial distribution of the grain-size of sediments on beaches in Guyana, is advanced here:

> Spatial variations in the concentrations of heavy metals are discernible and distinct in both across-shore and along-shore directions within accreting and eroding beaches.

While grain-size typically increases in a shoreward direction in the majority of coastal systems, it has been demonstrated by Cabana (1997) that accreting beaches, stable beaches or those that are in the early stages of erosion exhibit an inverse sediment distribution. In these types of coastal systems, the majority of nearshore sediments are clays and silty clays. Seaward of the band of clays and silty clays exists a very sandy surface of mixed sand, shell, and mud. Beaches that have been subjected to extensive erosion, however, display a more typical sediment distribution. Within the study area, grain-sizes were also discovered (Cabana, 1997) to decreases in an along-shore direction (westward) in both accreting and eroding beaches.

CHAPTER 3

3.1 Methodology:

3.1.1 Field Procedures:

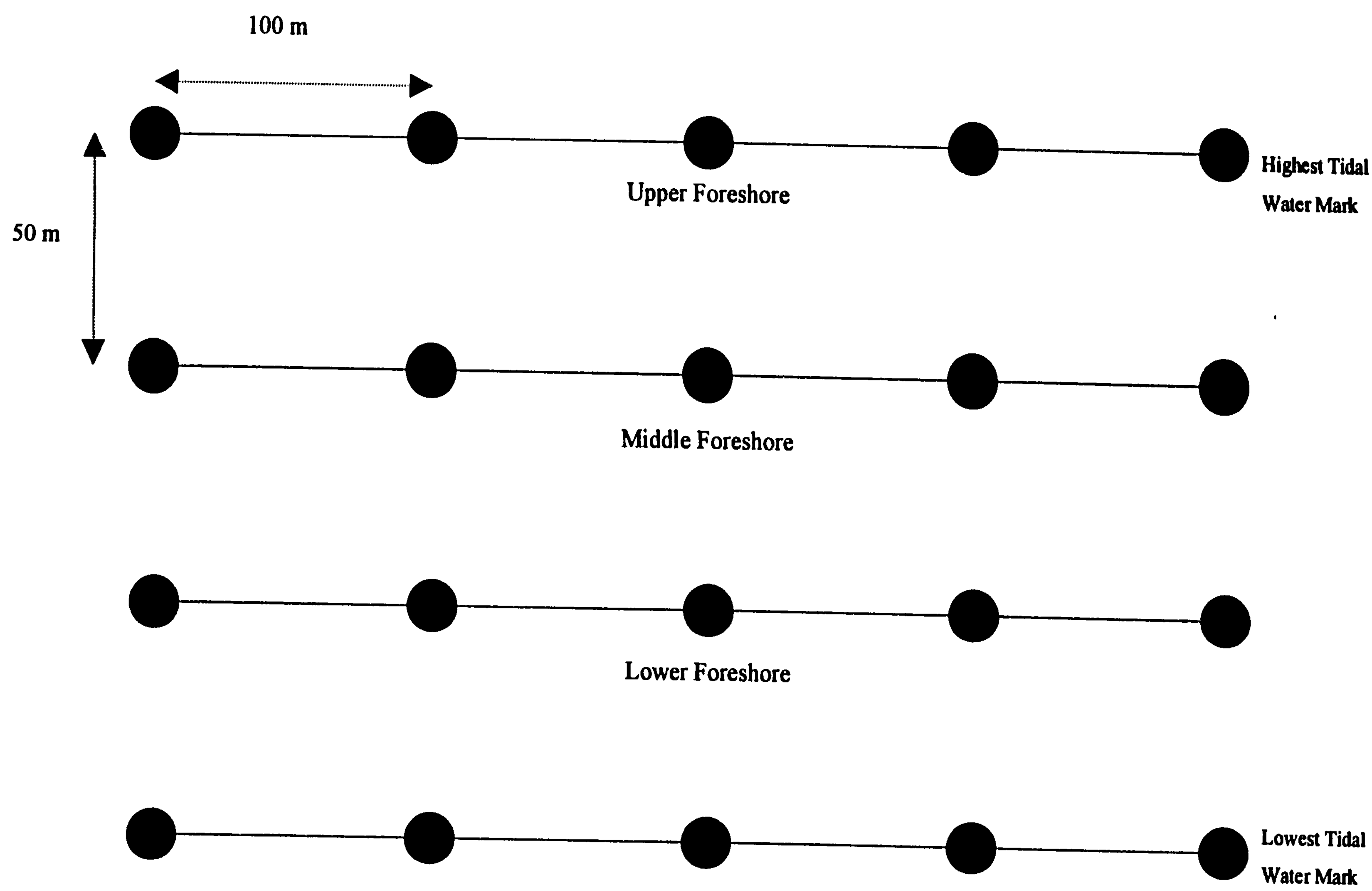
Sampling was systematically conducted in predetermined locations from accreting and eroding regions of the coast. At low tide, 12 samples were collected from each of the two regions at roughly 50 meter intervals in an across-shore direction and at 100 meter intervals in an along-shore direction (westward) (Figure 3.1). Sampling was also conducted in the nearshore, foreshore, and backshore zones of both regions. All samples were collected with the use of a sediment corer. Each of the collected samples weighed approximately 250 grams wet-weight. Individual samples were placed in sealed plastic bags and processed in the laboratory.

3.1.2 Laboratory Procedures:

In the laboratory, the sediment samples were oven-dried at 85 °C for two days in a Gallenkamp® OV-160 oven. Each day during the drying period, the sediment samples were mixed thoroughly to assist the drying process. Once dried, the samples were ground using a porcelain mortar and pestle. The porcelain mortar and pestle were cleaned thoroughly between each sample to ensure that cross contamination did not occur. All samples were weighed using a Mettler® PC440 scale.

Each 100 gram sample was then subjected to grain-size analysis using dry sieving methods. Nine sieves were used in this procedure including 2.0ϕ, 2.2ϕ, 2.4ϕ, 2.6ϕ, 2.8ϕ, 3.0ϕ, 3.5ϕ, 4.0ϕ and 5.0ϕ. Each 100 gram sample was placed in the stacked sieves and was subjected to one-half hour of sieving in a Ro-Tap sieve machine. Sediments of different grain-size were partitioned into each of the sieves during the sieving process.

Figure 3.1: Sampling Scheme



Source: Author (1998)

Upon completing the sieving procedures, the sediment in each sieve was weighed and recorded in a spreadsheet format (Appendix Table 1). The same procedures were repeated for each of the samples. It should be noted that the sieves used in the sieving process were read in metric units. However, for the sake of analysis, the sieve sizes were converted to Phi (ϕ) units using the following equation: $D = -\log_2(Dmm)$ (Folk and Ward, 1957) where D is the grain diameter in Phi (ϕ) units, and Dmm is the grain diameter in millimetres. With the Phi (ϕ) scale, as the Phi (ϕ) value increases the grain-size of the sediment decreases.

Grain-size analysis was conducted to allow the investigator to develop an understanding of the sedimentology of both beaches. Moreover, grain-size analysis was conducted to determine which grain fraction or fractions should be subjected to heavy metals analysis. Consultations with thesis advisors as well as the literature, in particular those studies conducted by Axtman *et al.* (1997), Ntekim *et al.* (1993), Fatimad *et al.* (1988), Rule (1986) and Salomons and Forstner (1984), resulted in the selection of the greater than 4.0 (ϕ) grain-size fraction. Thus, fractions 4.0 (ϕ), 5.0 (ϕ) and >5.0 (ϕ) were used in the heavy metals analysis. The greater than 4.0 (ϕ) fraction includes both silt and clay types of sediment.

For each sampling location, a small amount of sediment from the 4 (ϕ), 5 (ϕ) and > 5 (ϕ) sediment fractions and the 4 (ϕ) bulk sediment sample were submitted to the Great Lakes Institute for Environmental Research (GLIER), for heavy metals analysis. A total of 96 samples were submitted to GLIER. Analysis was conducted for the following metals: aluminum, copper, chromium, iron, nickel, vanadium, and zinc. To assess the samples for heavy metal concentrations, GLIER utilized the aquaregia, followed by inductively coupled plasma - optical emission spectroscopy (ICP-OES). This procedure involves the use of a Fissions Maxim Axial Plasma Spectrophotometer.

Aquaregia is the process of preparing the sample for injection into the ICP-OES. The protocol for sample preparation is outlined here:

> Weigh 1.0g of dry sample into a 125 mL Erlenmeyer flask. Add 10 mL of Nitric Acid and allow to stand at room temperature for 0.5-1 hours. To control foaming, an ice bath may be necessary. Next, add 20 mL of Hydrochloric Acid at room temperature and let stand for 1.0 hours. Again, to control foaming, an ice bath may be necessary. Following, the samples are then heated gradually on a hot plate to 100 °C for the remainder of the day, approximately 5.0 hours. The samples are continued to be heated overnight at 50 °C or until approximately 5mL acid is left (most do not go to dryness). In the event that this state is reached, add another 4mL of Aquaregia (1 mL Nitric and 3 mL Hydrochloric Acids) and heat for another hour. Transfer to dry pre-weighed 125 mL LDPE Nalgene bottles, filtering through Watman #4 or #41 filter paper. Rinse Erlenmeyer 5 times with P.W. during transfer. Make up solution to 100 g by weight to 0.01g. Exercise care to keep pre-weighed bottle dry during handling to avoid added error to solution final weight. (GLIER, 1996).

ICP involves the injection of a sample into a stream of argon gas, where it is carried into a plasma source that has been heated by a radio-frequency generator (Beaty and Kerber, 1993). Each sample is subjected to temperatures ranging from 6000-8000 K for approximately 2 msec. According to Skoog (1985), the ultraviolet-visible spectrum of the sample is monitored to detect the observed wavelengths. To determine the elements present in the sample as well as their concentrations, the observed wavelengths are compared to known wavelengths.

The results of the heavy metals analysis for the greater than 4.0 (ϕ) grain-size fraction can be viewed in Appendix Table 2. As well, the results of the heavy metals analysis for the 4.0 (ϕ), 5.0 (ϕ) and > 5.0 (ϕ) sediment groups are depicted in Appendix Tables 3 and 4.

3.2 Statistical Procedures:

3.2.1 Discriminant Analysis:

Discriminant analysis was utilized to assess the hypothesis that accreting beaches, with smaller grain-sizes and eroding beaches, with coarser grain-sizes exhibit contrasting concentrations of heavy metals. Discriminant analysis can be utilized to reveal populations of heavy metal concentrations that are statistically unique to each beach type. Discriminant analysis is a statistical method that produces hybrid variables so as to produce the best possible separation, or discrimination, between the various groups (Johnston, 1992). In other words, linear combinations of the independent variable, or predictor variables are formed and serve as the basis for classifying cases into one of the groups.

Since the objective of the executions of discriminant analysis was to determine whether the accreting and eroding beaches differ significantly in terms of heavy metal concentrations, the two beaches (Albion and Melanie) were entered as the grouping variable. The heavy metal concentrations of the metals under investigation were entered as the independent variables. The heavy metal concentrations utilized were those for the > 4 (ϕ) bulk sediment samples for each beach. Eight separate executions of the program were performed. SPSS® version 9 for Windows® was used for all executions of discriminant analysis.

3.2.2 Line Graphs:

Two separate series of line graphs were constructed to assess the hypothesis that spatial variations in the concentrations of heavy metals are discernible and distinct in both across-shore and along-shore directions (westward) within accreting and eroding beaches.

The concentrations of each of the heavy metals under investigation for the > 4.0 (ϕ) bulk sediment fraction (Y) were plotted against the across-shore sampling locations (X) in the first series of line graphs. This was done for each of the two beaches. Thus, sixteen line graphs were produced within the first series. Sixteen line graphs were also produced within the second series of line graphs. For this series of line graphs, the concentrations of the heavy metals (Y) under investigation for the > 4 (ϕ) bulk sediment fraction were plotted against the along-shore sampling locations (X). All line graphs were constructed with the use of Microsoft Excel ® version 7.0.

3.2.3 Analysis of Variance:

Like discriminant analysis, analysis of variance is a statistical test used to ascertain if places differ in terms of the phenomena present there. In addition to ascertaining whether places differ in terms of the phenomena present there, analysis of variance reveals behavioural differences or similarities among the phenomena. Analysis of variance was used in this investigation to provide support to the results of discriminant analysis, and more importantly, to ascertain if the concentrations of the heavy metals under study behaved differently within Albion and Melanie beaches.

The analysis of variance was conducted in two stages. The first stage involved conducting a multiple or two-way analysis of variance while the second stage involved performing separate one-way analyses for each beach. In addition to shaping the second stage, the results of the multiple analysis of variance also dictated the approach that needed to be taken when performing the correlation and regression analysis. SPSS® version 9 for Windows® was used for all executions of analysis of variance.

3.2.4 Correlation and Regression Analysis:

In order to ensure that the results of the hypothesis evaluations were based upon the premise that grain-size is the primary variable controlling the distribution of heavy metals, correlation and regression analysis was performed. Correlation analysis is a statistical test that measures the strength and significance of a relationship. Correlation analysis relates the variance in the dependent variable (Y) to the reduction in that variance when the independent variable (X) is used to estimate values of the dependent variable (Y). Regression analysis is a statistical test that measures the sensitivity and direction of a relationship. Essentially, regression analysis measures the amount of change in the dependent variable (Y) for a given change in the independent variable (X).

With the use of correlation and regression analysis, several types of curve estimations may be performed by the investigator. The curve estimation of choice for this investigation was quadratic. Although grain-size class in this investigation is represented as a discrete categorical variable which is associated with the use of mechanical analysis, one can safely assume that in reality grain-size data are characterized by a continuum of particle sizes. If individual particle sizes could be economically measured and correlated to heavy metal concentration levels, then one would probably be dealing with continuous variables making quadratic regression equations the most appropriate selection. For all curve estimations, the grain-size of sediment in Phi (ϕ) units was entered as the independent variable (X) and the natural logarithms of the heavy metal concentrations for each of the metals of concern were entered as the dependent variables. Both correlation and regression analysis were conducted with the use of SPSS® version 9.0 for Windows®.

CHAPTER 4

4.1 Analytic Findings

4.1.1 Discriminant Analysis Results:

Discriminant analysis was used to reveal heavy metal concentrations statistically unique to each beach type. For the linear discriminant function to be "optimal" – that is to provide a classification rule that minimizes the probability of misclassification- certain assumptions about the data must be met. First, each group must be a sample from a multivariate normal population. Second, the population covariances must all be equal. The data utilized in all eight executions of discriminant analysis did not violate either of these two assumptions.

The results of the executions of the discriminant analysis program are depicted in Figures 4.1- 4.8. Each execution of the program was assessed individually. All assessments of each individual execution of the program were made based on three essential statistics. These statistics include the canonical correlation statistic, the Wilk's lambda or the U statistic and significance. The canonical correlation statistic associates the discriminant function with the dependent variable (the grouping of the observations). This correlation is analogous to the squared product moment correlation. Essentially, the canonical correlation statistic indicates the ratio of between-group to total variance estimates along the discriminant function. Thus, the larger the canonical correlation statistic is, the greater is the between-groups variation as a proportion of the total variation. The Wilk's lambda or the U statistic is a measure, which indicates the within-group variance to the total variance estimates along the discriminant function. The larger the Wilk's lambda statistic is, the greater is the within-group variation as a proportion of the total variation and the greater successful is the discriminant function at separating the groups. The Wilk's lambda statistic is an inverse of the F-ratio; it can also be transformed into a chi-square value and used to test the statistical significance of the discriminant function.

Figure 4.1 illustrates the results of the discriminant analysis execution for aluminum. This execution yielded a high canonical correlation value (0.816). Thus, a high degree of between-group variations exist. Within-group variations are low in terms of the total variations between the two beaches as evidenced by the low Wilk's lambda value (0.334). Moreover, both the canonical correlation and the Wilk's lambda statistics are significant. In terms of the discriminant function, 95.8 % of the original grouped cases were correctly classified. A graphical representation of the discriminant scores provides further evidence that the two beaches differ significantly in terms of their heavy metal concentrations of aluminum.

Similar results were produced by the discriminant analysis execution for chromium (Figure 4.2). Both the canonical correlation (0.858) and the Wilk's lambda (0.263) statistics were statistically significant. As evidenced by these statistics, a high degree of between-group variations and a low degree of within-group variations exist between the two beach types. Of the originally grouped cases, 91.7 % were correctly classified. A further illustration of the differences between the two beach types in terms of their concentrations of the heavy metal chromium is rendered by the graphical representation of the discriminant scores.

The results of the discriminant analysis execution for tcopper are depicted in Figure 4.3. From Figure 4.3, it is evident from the canonical correlation

Figure 4.1: Discriminant Analysis Results for Aluminum - Restrictive Grain Fraction

Eigenvalues

Function	Eigenvalue	% of Variance	Cumulative e %	Canonical Correlation
1	1.992ª	100.00	100.00	0.816

Wilks' Lambda

Test of Function(s)	Wilks' Lambda	Chi-Square	df	Signifigance
1	0.334	23.565	1	0.000

95.8 % of original grouped cases correctly classified

All-groups Stacked Histogram Canonical Discriminant Function 1 - Aluminum

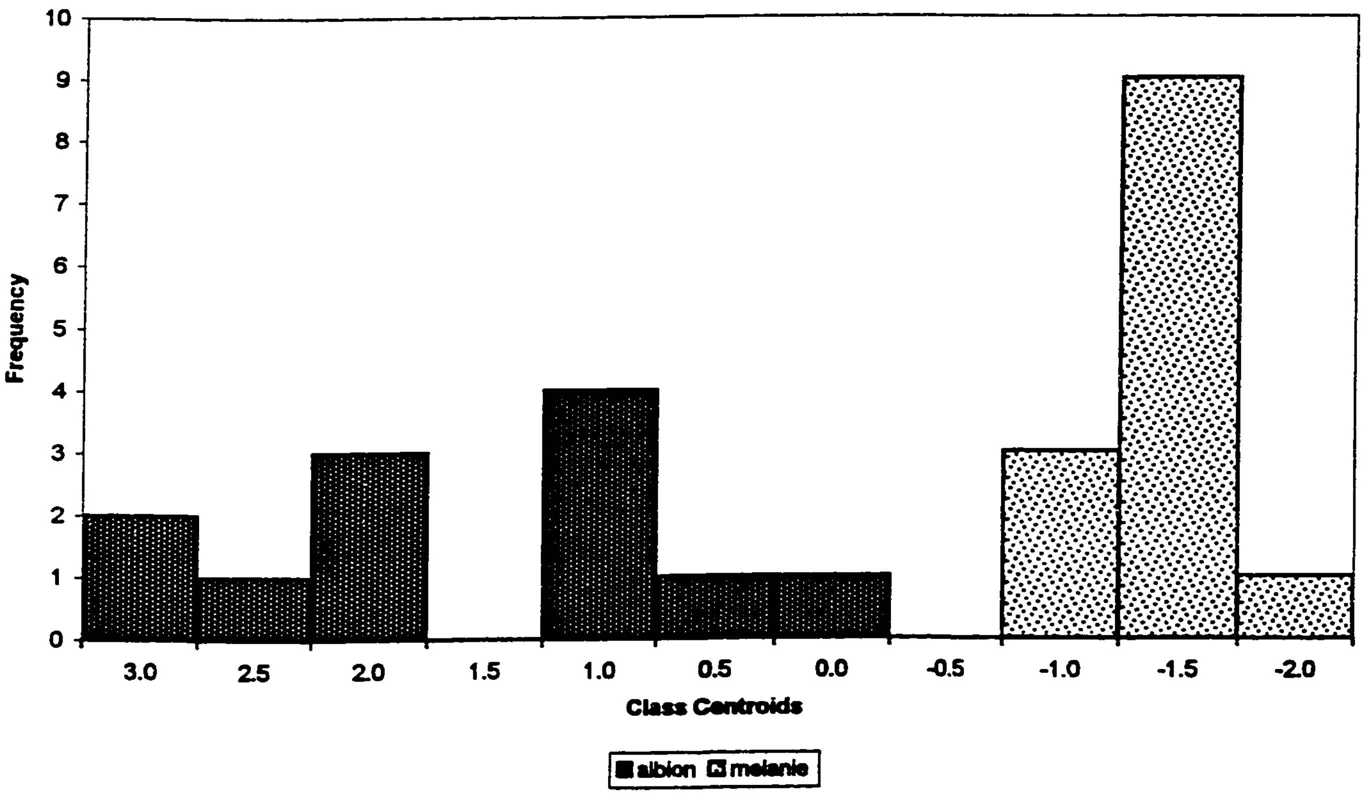


Figure 4.2: Discriminant Analysis Results for Chromium - Restrictive Grain Fraction

Eigenvalues

Function	Eigenvalue	% of Variance	Cumulative e %	Canonical Correlation
1	2.796[a]	100.00	100.00	0.858

Wilks' Lambda

Test of Function(s)	Wilks' Lambda	Chi-Square	df	Signifigance
1	0.263	28.681	1	0.000

91.7% of original grouped cases correctly classified

All-groups Stacked Histogram Canonical Discriminant Function 1 - Chromium

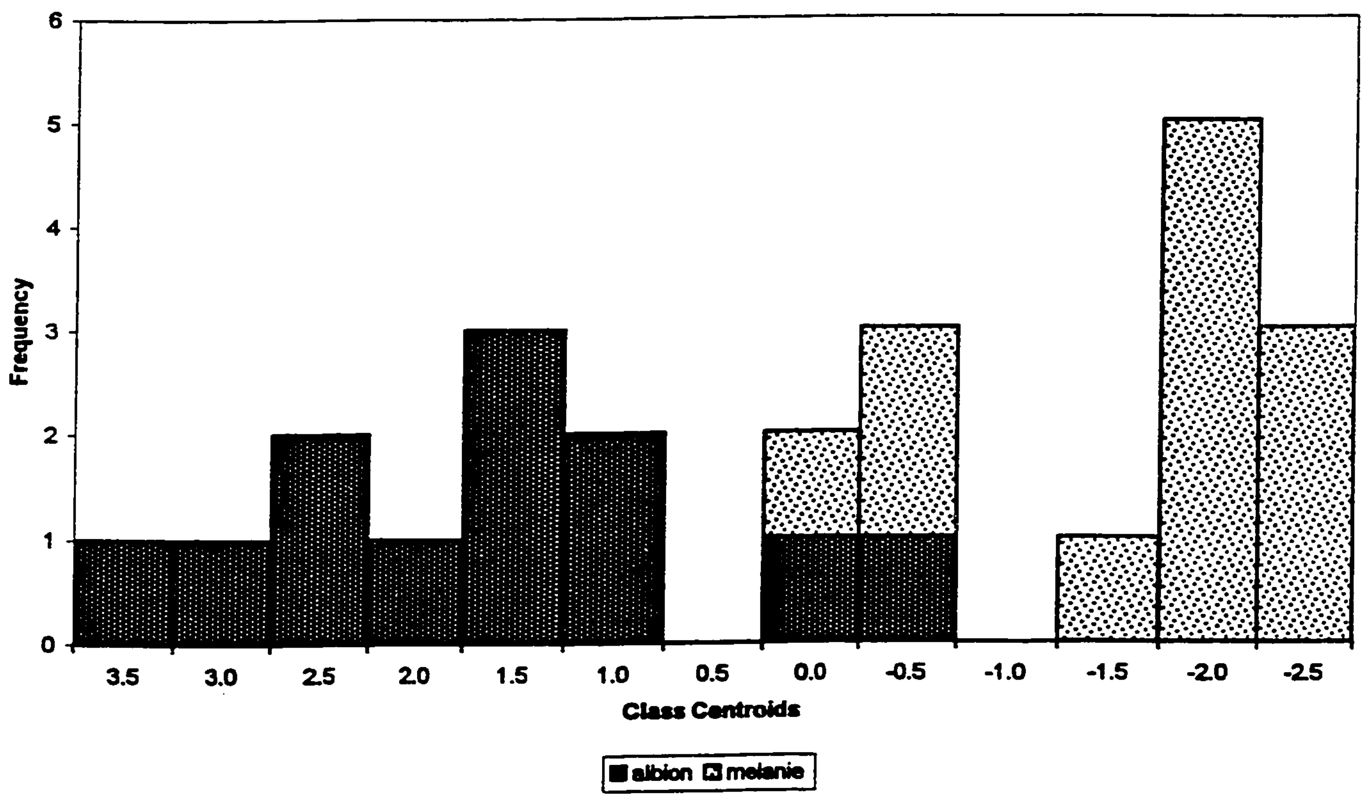


Figure 4.3: Discriminant Analysis Results for Copper - Restrictive Grain Fraction

Eigenvalues

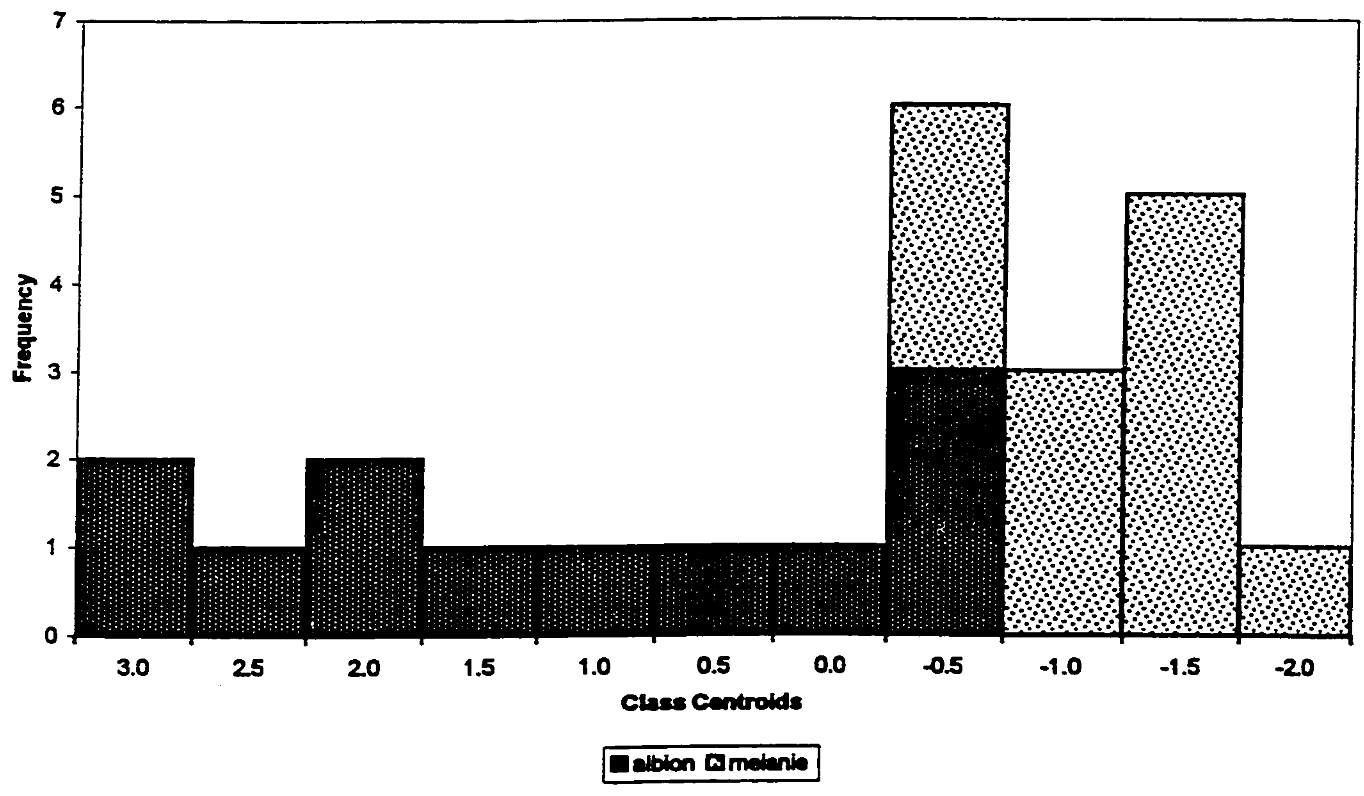
Function	Eigenvalue	% of Variance	Cumulative %	Canonical Correlation
1	1.598[a]	100.00	100.00	0.784

Wilks' Lambda

Test of Function(s)	Wilks' Lambda	Chi-Square	df	Signifigance
1	0.385	20.525	1	0.000

87.5% of original grouped cases correctly classified

All-groups Stacked Histogram Canonical Discriminant Function 1 - Copper



statistic (0.784) that a high degree of between-group variations exist. Within-group variations are small as evidenced by the relatively low Wilk's lambda statistic (0.385). Both of these statistics are significant. The percentage of correctly classified cases from the original groups is 87.5 %. The statistically significant between-group variations are further noticeable in the graphical representation of the discriminant scores.

The between-group variation, among the two beach types, with respect to the heavy metal iron (Figure 4.4) is not as pronounced as the previous three elements. This is evidenced by the canonical correlation value of 0.638. The between-group variation is best described as moderate and is nevertheless, statistically significant. A moderate level of within-group variation also exists as evidenced by the Wilk's lambda statistic (0.593). This statistic is also significant. A graphical representation of the discriminant scores for each sample from each beach type further illustrates that the two beaches are unique in terms of their concentrations of the heavy metal iron. The percentage of the original grouped cases that were correctly classified based on the discriminant functions was 95.8.

The results of the discriminant analysis execution for nickel are depicted in Figure 4.5. The canonical correlation statistic and the Wilk's lambda statistic yielded by the test were 0.929 and 0.138 respectively. Evidently, an extremely high amount of between-group variations and an extremely low amount of within-group variations exist. One hundred percent of the original grouped cases were correctly classified as per the discriminant functions. Absolutely no overlapping among the discriminant scores occurred.

High levels of between-group and moderate levels of within-group variations were produced by the discriminant analysis execution for lead (Figure 4.6). This is evident from

Figure 4.4: Discriminant Analysis Results for Iron - Restrictive Grain Fraction

Eigenvalues

Function	Eigenvalue	% of Variance	Cumulative e %	Canonical Correlation
1	.685[a]	100.00	100.00	0.638

Wilks' Lambda

Test of Function(s)	Wilks' Lambda	Chi-Square	df	Signifigance
1	0.593	11.219	1	0.000

95.8% of original grouped cases correctly classified

All-groups Stacked Histogram Canonical Discriminant Function 1 - Iron

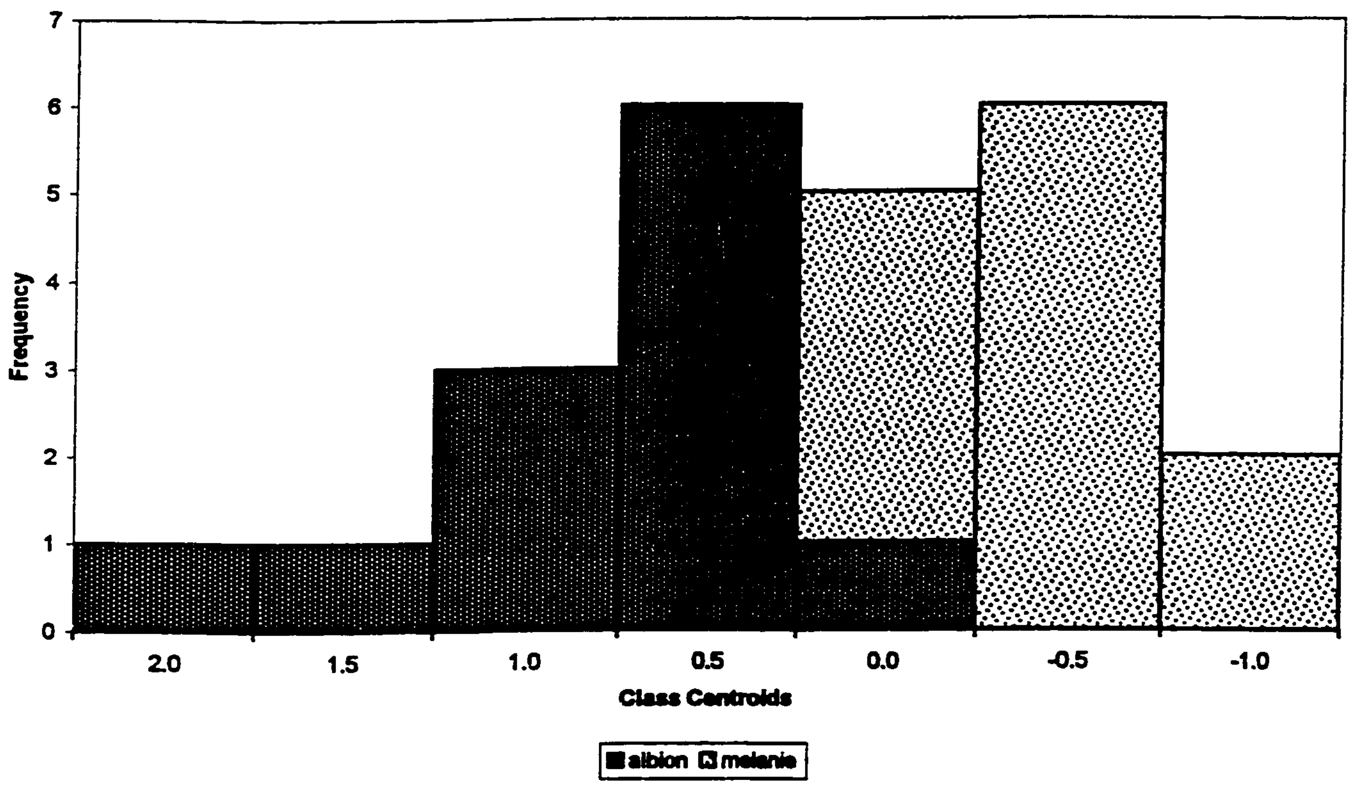


Figure 4.5: Discriminant Analysis Results for Nickel - Restrictive Grain Fraction

Eigenvalues

Function	Eigenvalue	% of Variance	Cumulative e %	Canonical Correlation
1	6.254[a]	100.00	100.00	0.929

Wilks' Lambda

Test of Function(s)	Wilks' Lambda	Chi-Square	df	Signifigance
1	0.138	42.605	1	0.000

100 % of original grouped cases correctly classified

All-groups Stacked Histogram Canonical Discriminant Function 1 - Nickel

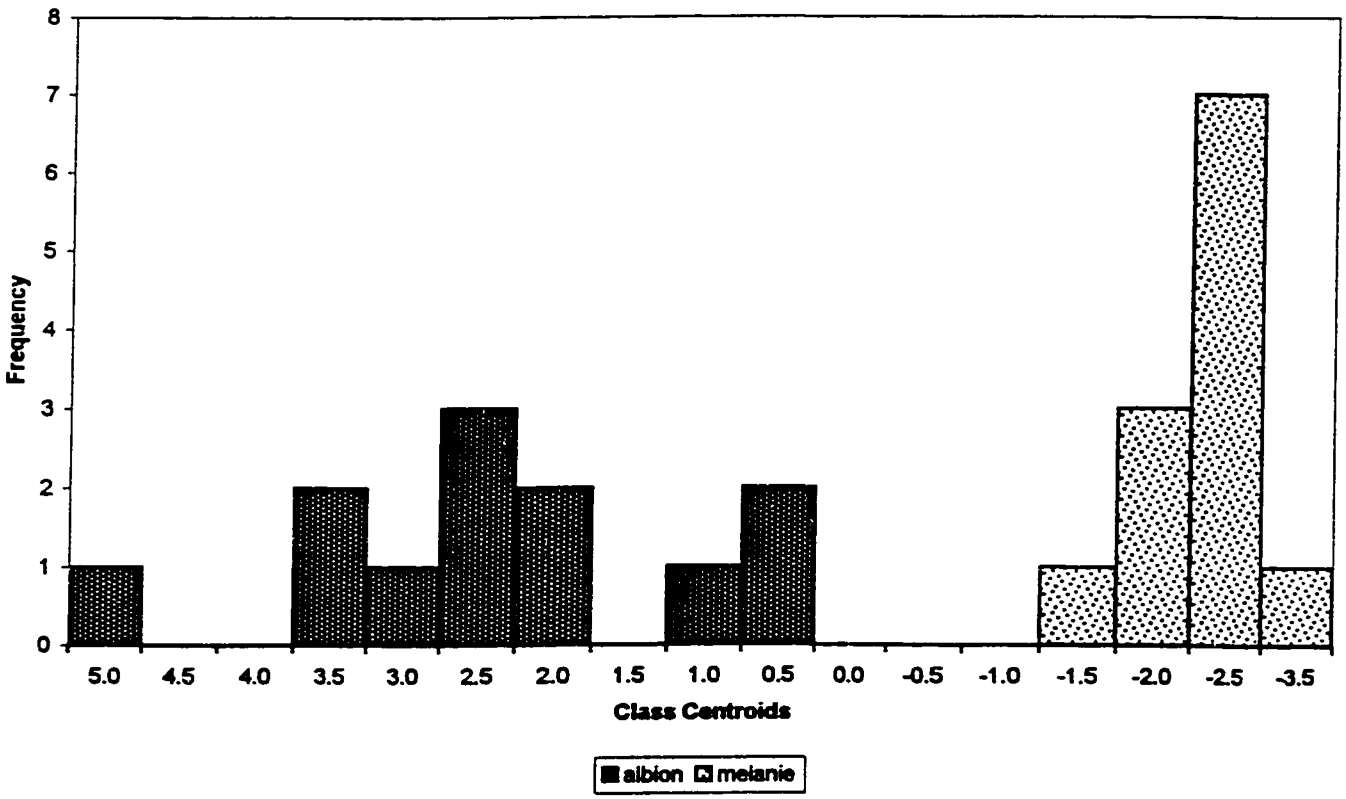


Figure 4.6: Discriminant Analysis Results for Lead - Restrictive Grain Fraction

Eigenvalues

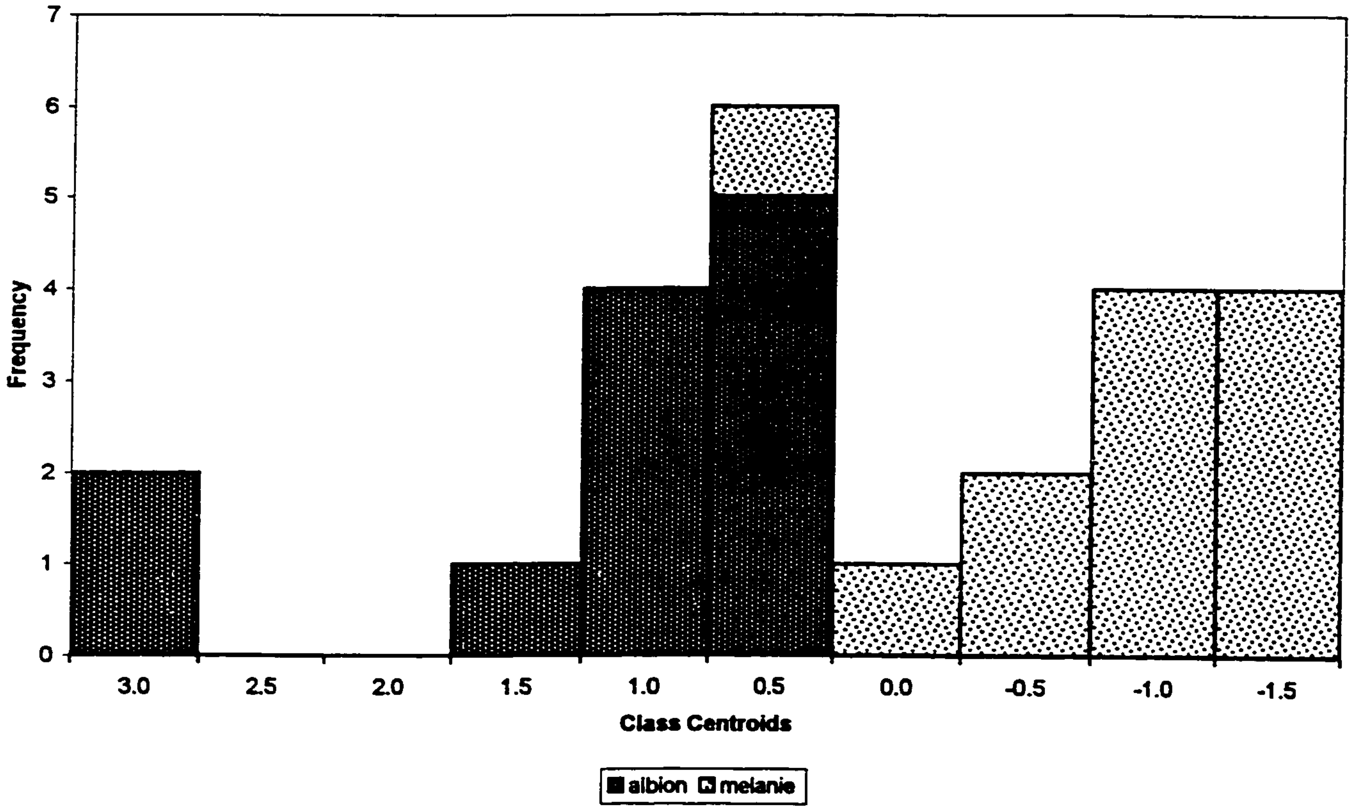
Function	Eigenvalue	% of Variance	Cumulative %	Canonical Correlation
1	1.011[a]	100.00	100.00	0.709

Wilks' Lambda

Test of Function(s)	Wilks' Lambda	Chi-Square	df	Signifigance
1	0.497	15.017	1	0.000

83.3% of original grouped cases correctly classified

All-groups Stacked Histogram Canonical Discriminant Function 1 - Lead



the canonical correlation statistic (0.709) and the Wilk's lambda statistic (0.497). Of the original grouped cases 83.3 % were correctly classified. A further illustration of the differences between the two beach types in terms of their concentrations of the heavy metal lead is rendered by the graphical representation of the discriminant scores.

The results from the discriminant analysis execution for vanadium (Figure 4.7) also depict high levels of between-group variation and moderate levels of within-group variation. This is evidenced by the canonical correlation and Wilk's lambda statistics of 0.693 and 0.520 respectively. A lower amount (76.2 %) of the original grouped cases than for the rest of the metals was correctly classified with respect to the discriminant functions. Some overlap among the cases of the canonical discriminant function exists as evidenced by their graphical representation.

The discriminant analysis execution results for zinc are depicted in Figure 4.8. The canonical correlation statistic of 0.778 indicates that a high degree of between-group variation exists between the two beach types. A low degree of within-group variation exists between the two beach types as evidenced by the Wilk's lambda value of 0.395. The percentage of the original grouped cases that were correctly classified was 91.7. Low levels of overlap among the cases of the canonical discriminant function exist as seen in the all-groups stacked histogram within Figure 4.8.

Figure 4.7: Discriminant Analysis Results for Vanadium - Restrictive Grain Fraction

Eigenvalues

Function	Eigenvalue	% of Variance	Cumulative %	Canonical Correlation
1	0.922[a]	100.00	100.00	0.693

Wilks' Lambda

Test of Function(s)	Wilks' Lambda	Chi-Square	df	Signifigance
1	0.52	12.088	1	0.000

76.2 % of original grouped cases correctly classified

All-groups Stacked Histogram Canonical Discriminant Function 1 - Vanadium

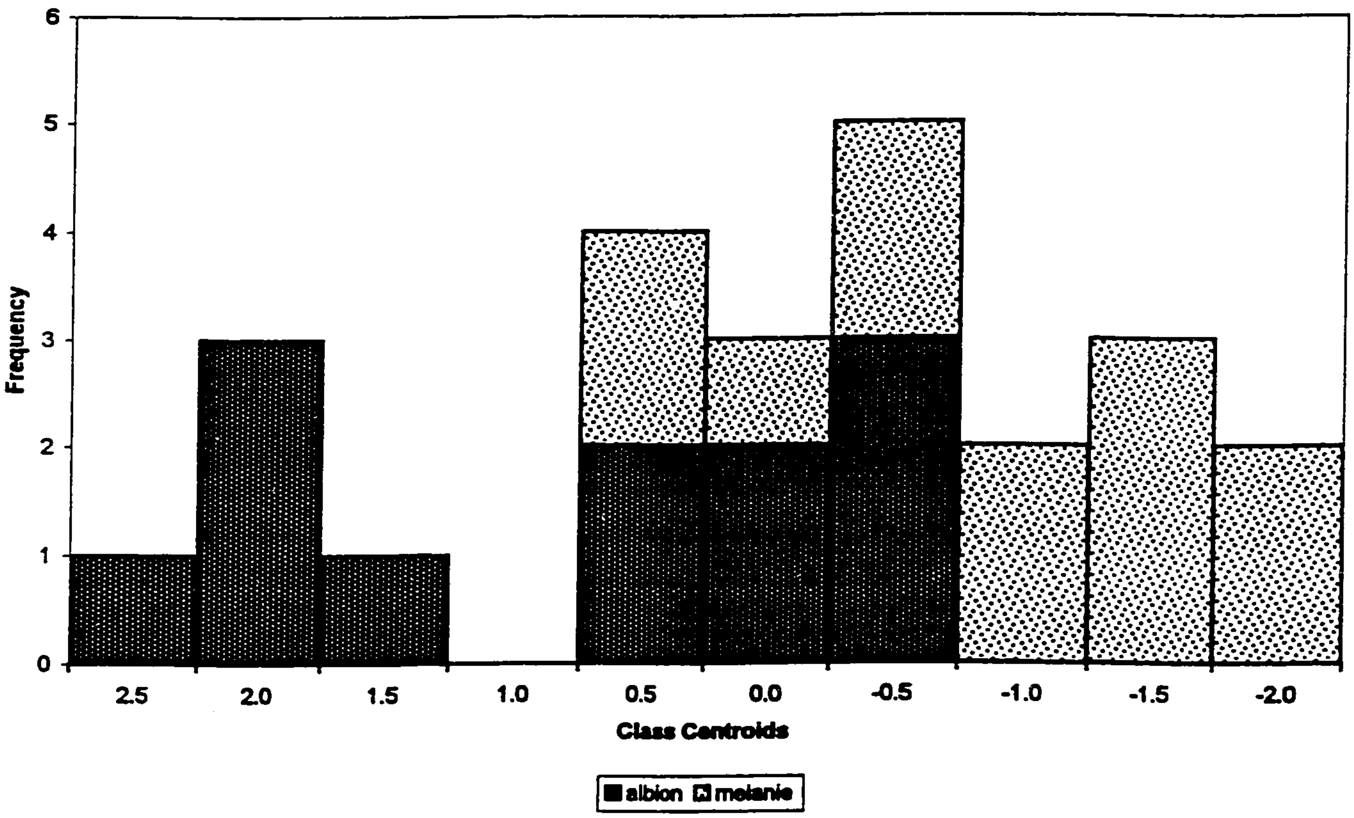


Figure 4.8: Discriminant Analysis Results for Zinc - Restrictive Grain Fraction

Eigenvalues

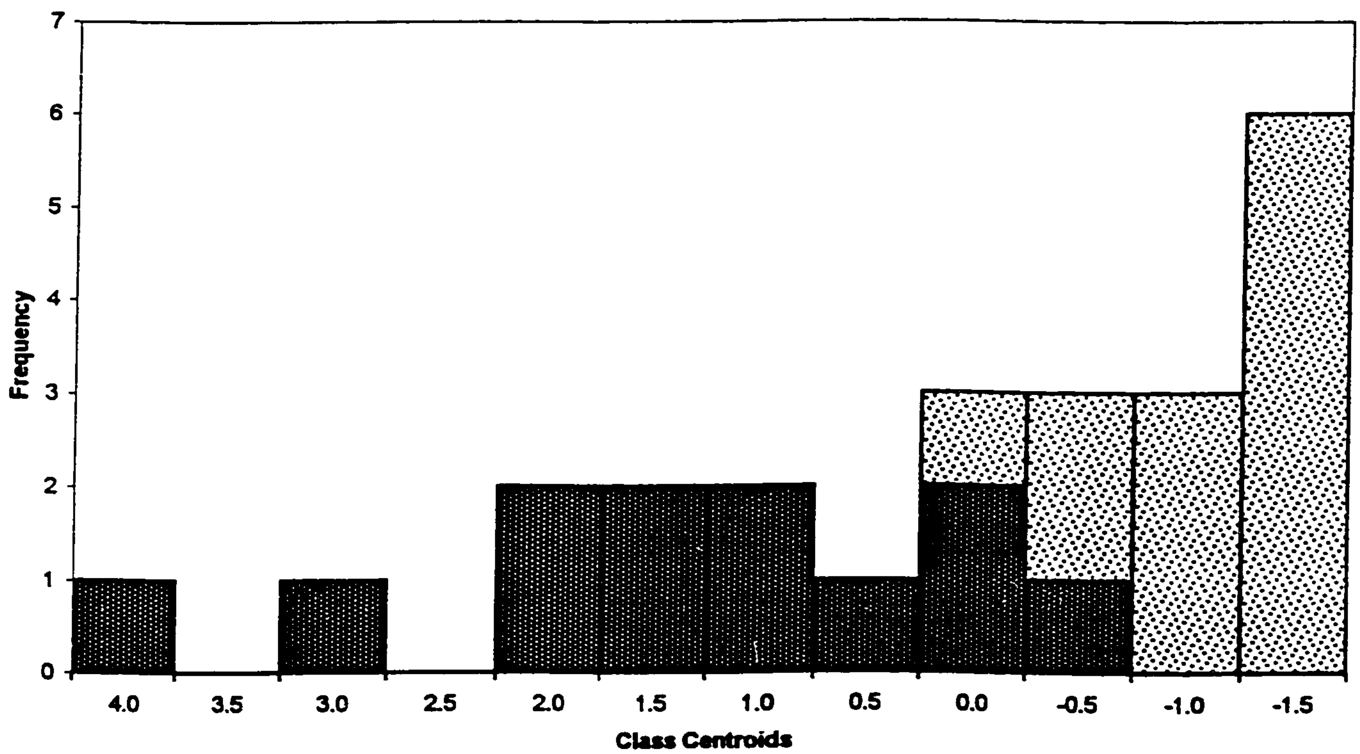
Function	Eigenvalue	% of Variance	Cumulat-ive e %	Canonical Correlation
1	1.532[a]	100.00	100.00	0.778

Wilks' Lambda

Test of Function(s)	Wilks' Lambda	Chi-Square	df	Signifigance
1	0.395	19.975	1	0.000

91.7% of original grouped cases correctly classified

All-groups Stacked Histogram Canonical Discriminant Function 1 - Zinc



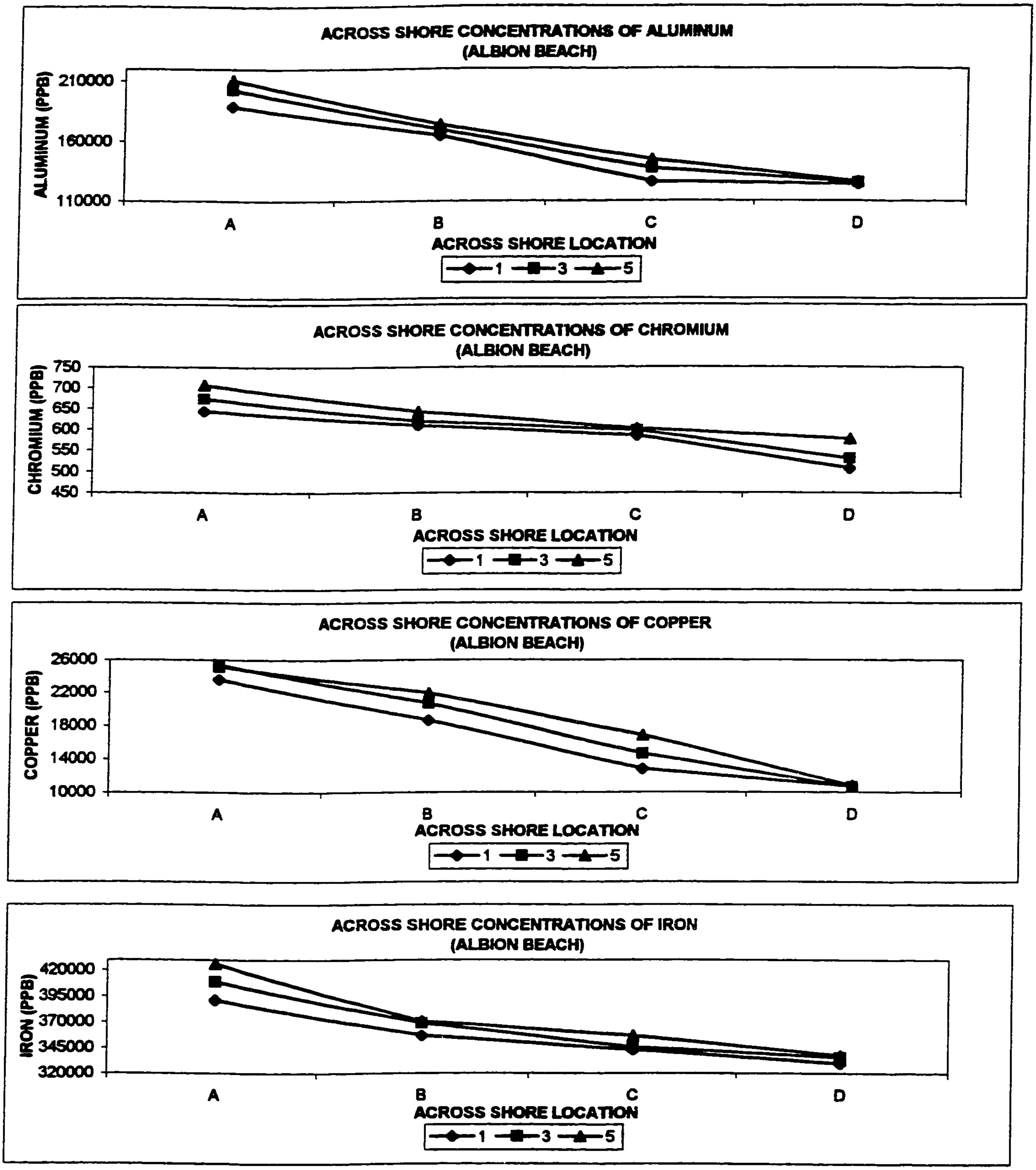
4.1.2 Line Graph Results:

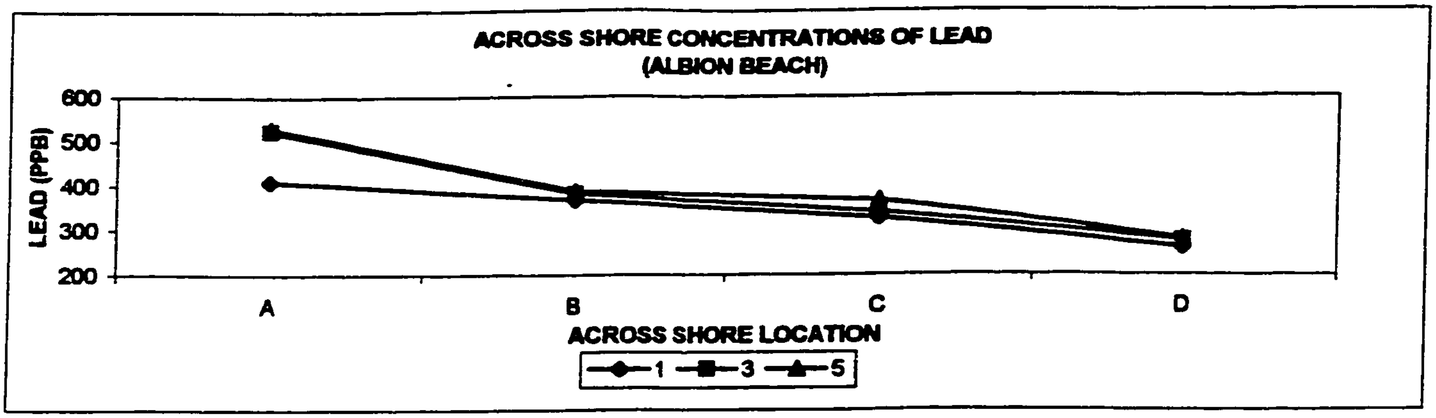
Despite being a simplistic tool, two separate series of line graphs were utilized to determine if spatial variations in the concentrations of heavy metals are discernible and distinct in both across-shore and along-shore directions (westward) within accreting and eroding beaches. Two series of line graphs for each beach type have been constructed. These series include one that depicts metal concentrations in an across-shore direction and the other which depicts metal concentrations in an along-shore direction.

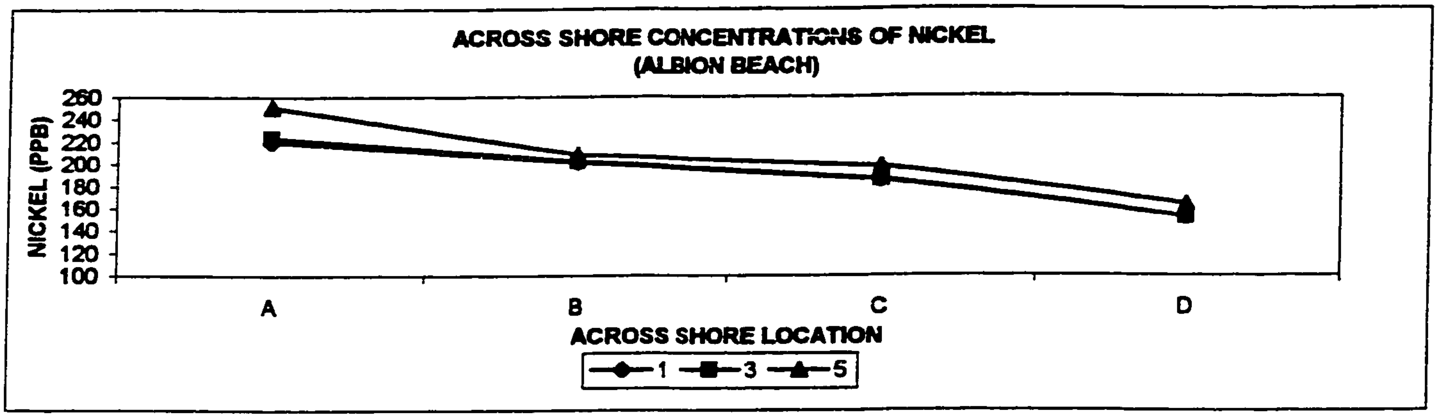
Figures 4.9 and 4.10 graphically display across-shore concentrations of heavy metals for Albion and Melanie beaches respectively. The data for these concentrations are depicted in Appendix Table 5. From Table 4.9 and Appendix Table 5 it is evident that within Albion beach the concentrations of heavy metals for all metal types increase in a shoreward direction. This is true in 24 of 24 cases. From Figure 4.10 and Appendix Table 5 it is apparent that within Melanie beach the concentrations of heavy metals for all metal types decrease in a shoreward direction. This is also true in 24 of 24 cases.

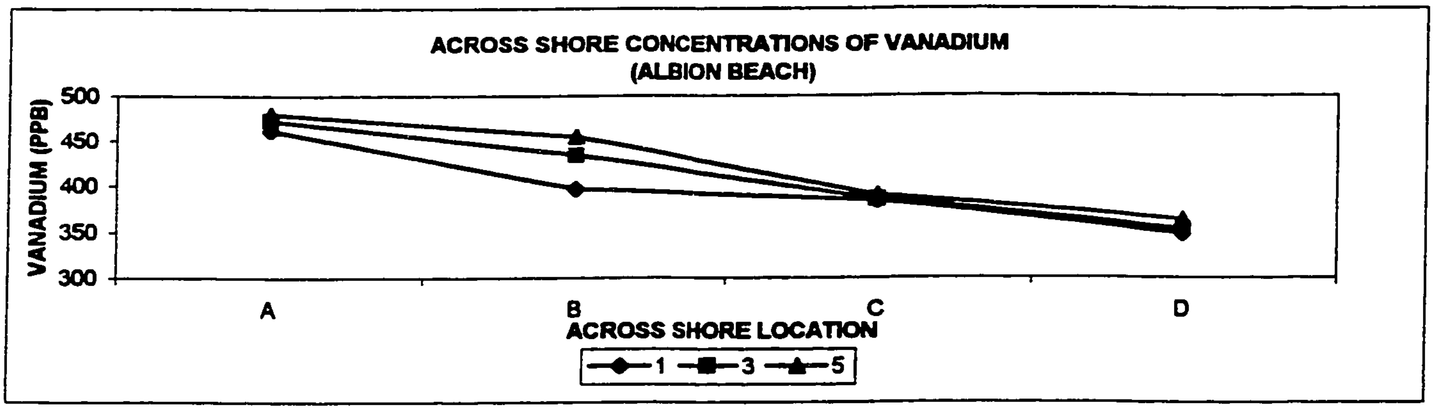
Figures 4.11 and 4.12 as well as Appendix Table 6 display along-shore concentrations of heavy metals for Albion and Melanie beaches graphically and numerically respectfully. From Figure 4.11 and Appendix Table 6 it is apparent that within Albion beach the concentrations of heavy metals for all metal types in the majority of cases increase in an along-shore direction (westward). This is true in 27 of 32 or 84 % of the cases. Similarly, from Figure 4.12 and Appendix Table 6 it is evident that within Melanie beach the concentrations of heavy metals for all metal types in the majority of cases increase in an along-shore direction (westward). This is true in 26 of 32 or 81 % of the cases.

Figure 4.9: Across-Shore Concentrations of Heavy Metals (Albion Beach)




ACROSS SHORE CONCENTRATIONS OF LEAD
(ALBION BEACH)
LEAD (PPB)
600
500
400
300
200
A
B
C
D
ACROSS SHORE LOCATION
1
3
5


ACROSS SHORE CONCENTRATIONS OF NICKEL
(ALBION BEACH)
NICKEL (PPB)
260
240
220
200
180
160
140
120
100
A
B
C
D
ACROSS SHORE LOCATION
1
3
5


ACROSS SHORE CONCENTRATIONS OF VANADIUM
(ALBION BEACH)
VANADIUM (PPB)
500
450
400
350
300
A
B
C
D
ACROSS SHORE LOCATION
1
3
5

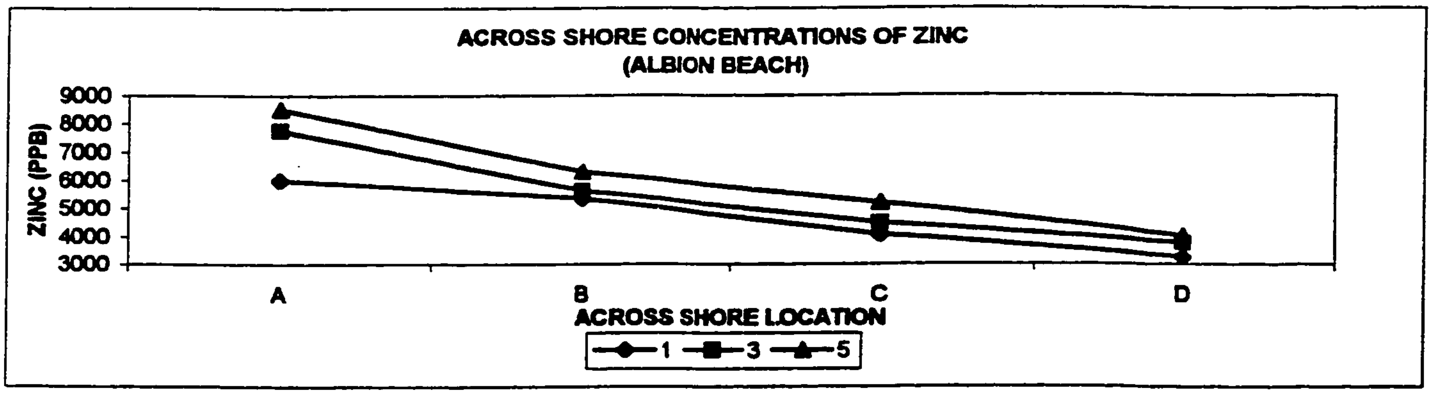
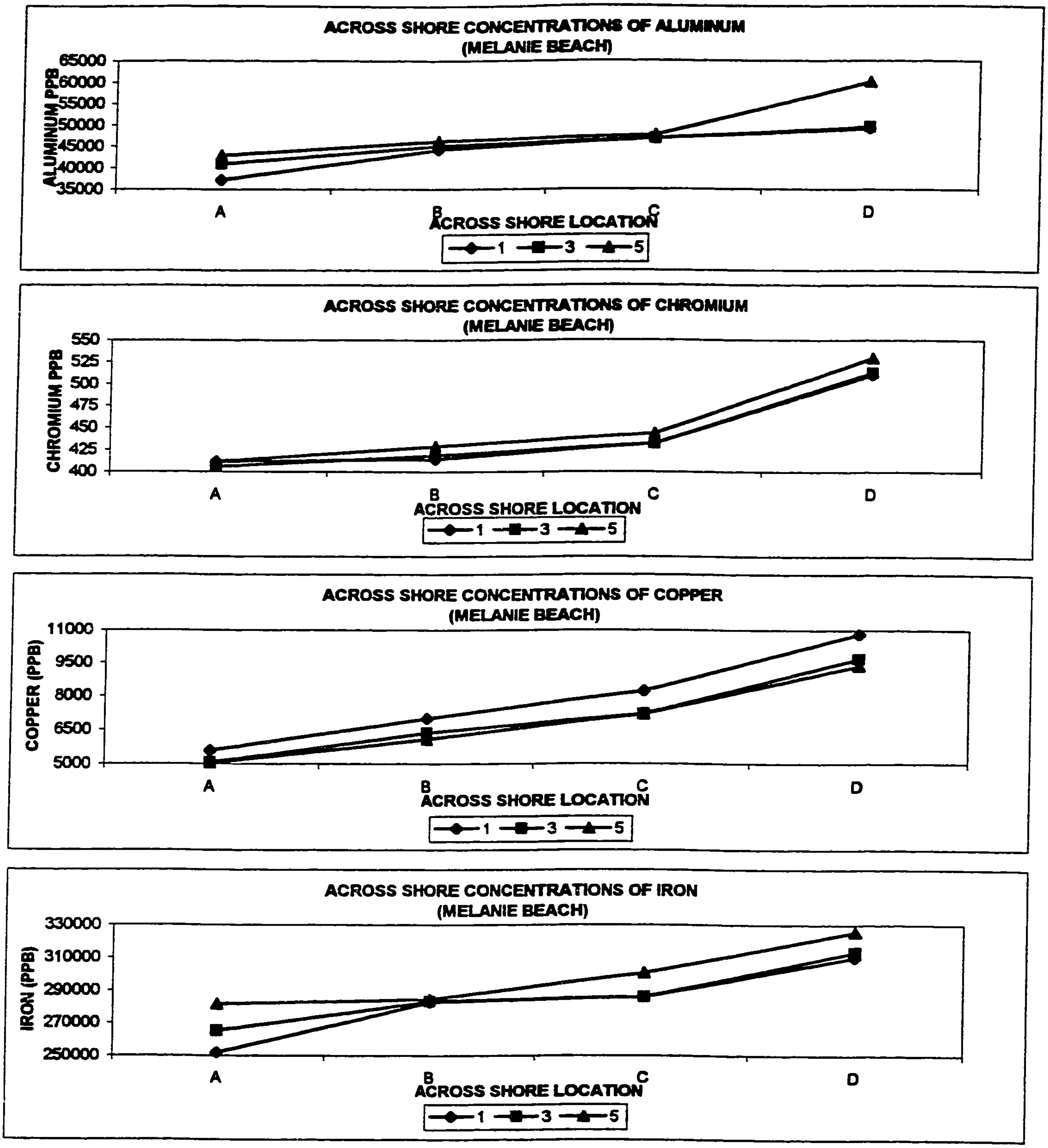
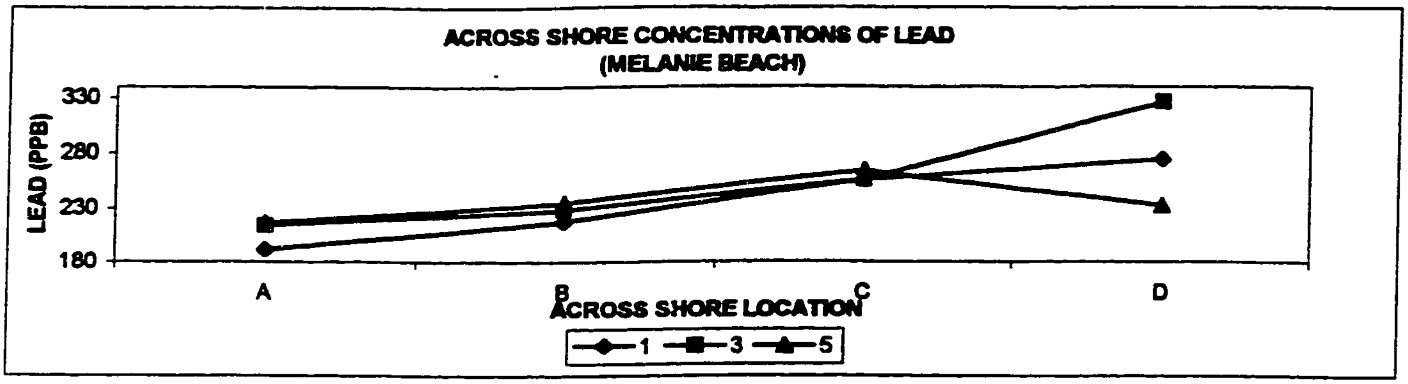
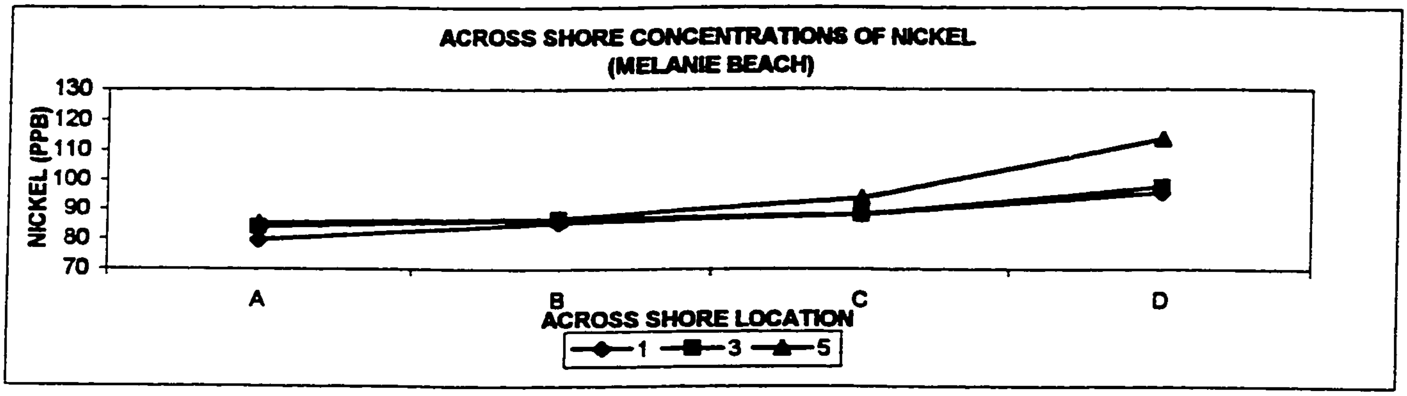
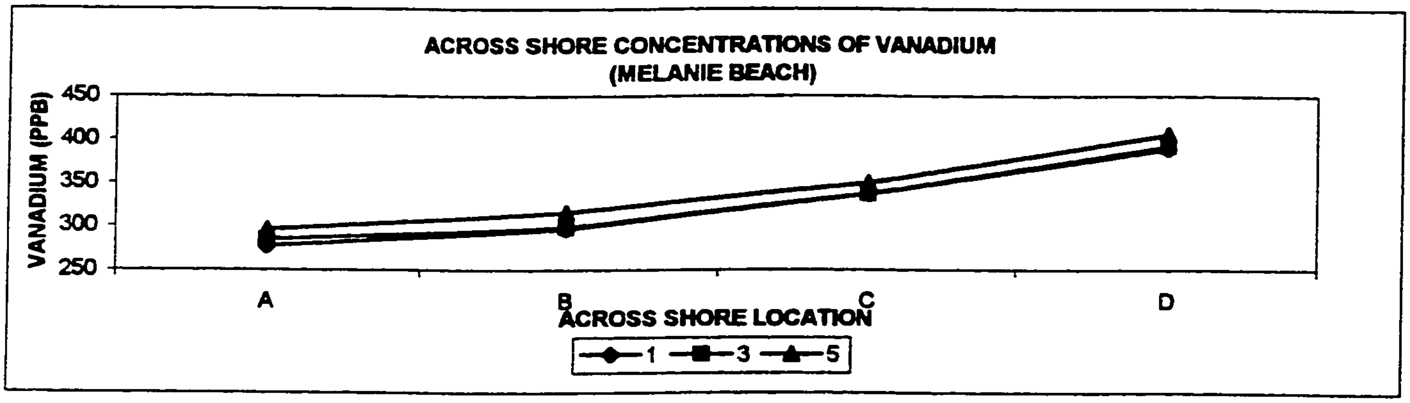

ACROSS SHORE CONCENTRATIONS OF ZINC
(ALBION BEACH)
ZINC (PPB)
9000
8000
7000
6000
5000
4000
3000
A
B
C
D
ACROSS SHORE LOCATION
1
3
5

Figure 4.10: Across-Shore Concentrations of Heavy Metals (Melanie Beach)




ACROSS SHORE CONCENTRATIONS OF LEAD
(MELANIE BEACH)
LEAD (PPB)
330
280
230
180
A
B
C
D
ACROSS SHORE LOCATION
1
3
5


ACROSS SHORE CONCENTRATIONS OF NICKEL
(MELANIE BEACH)
NICKEL (PPB)
130
120
110
100
90
80
70
A
B
C
D
ACROSS SHORE LOCATION
1
3
5


ACROSS SHORE CONCENTRATIONS OF VANADIUM
(MELANIE BEACH)
VANADIUM (PPB)
450
400
350
300
250
A
B
C
D
ACROSS SHORE LOCATION
1
3
5

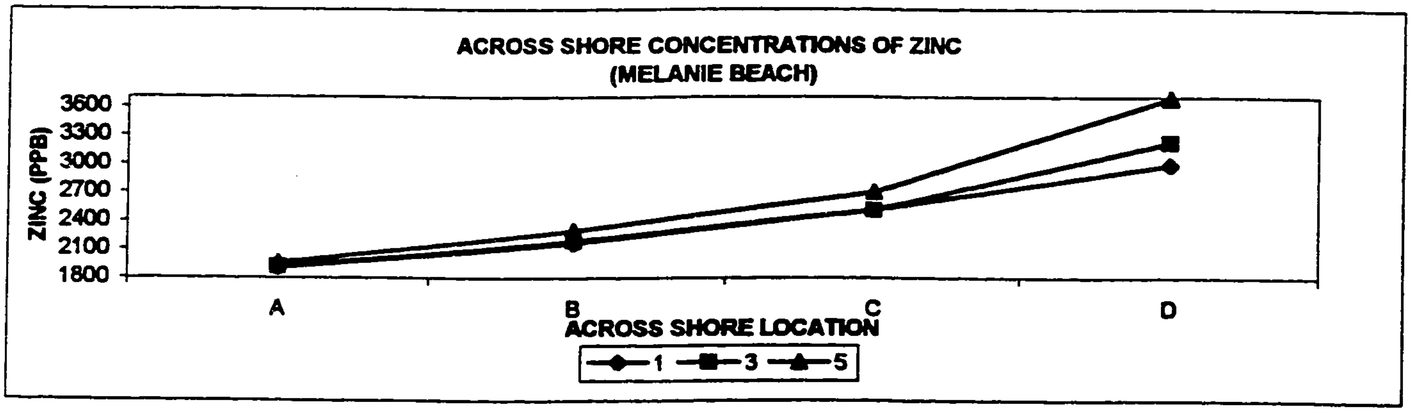
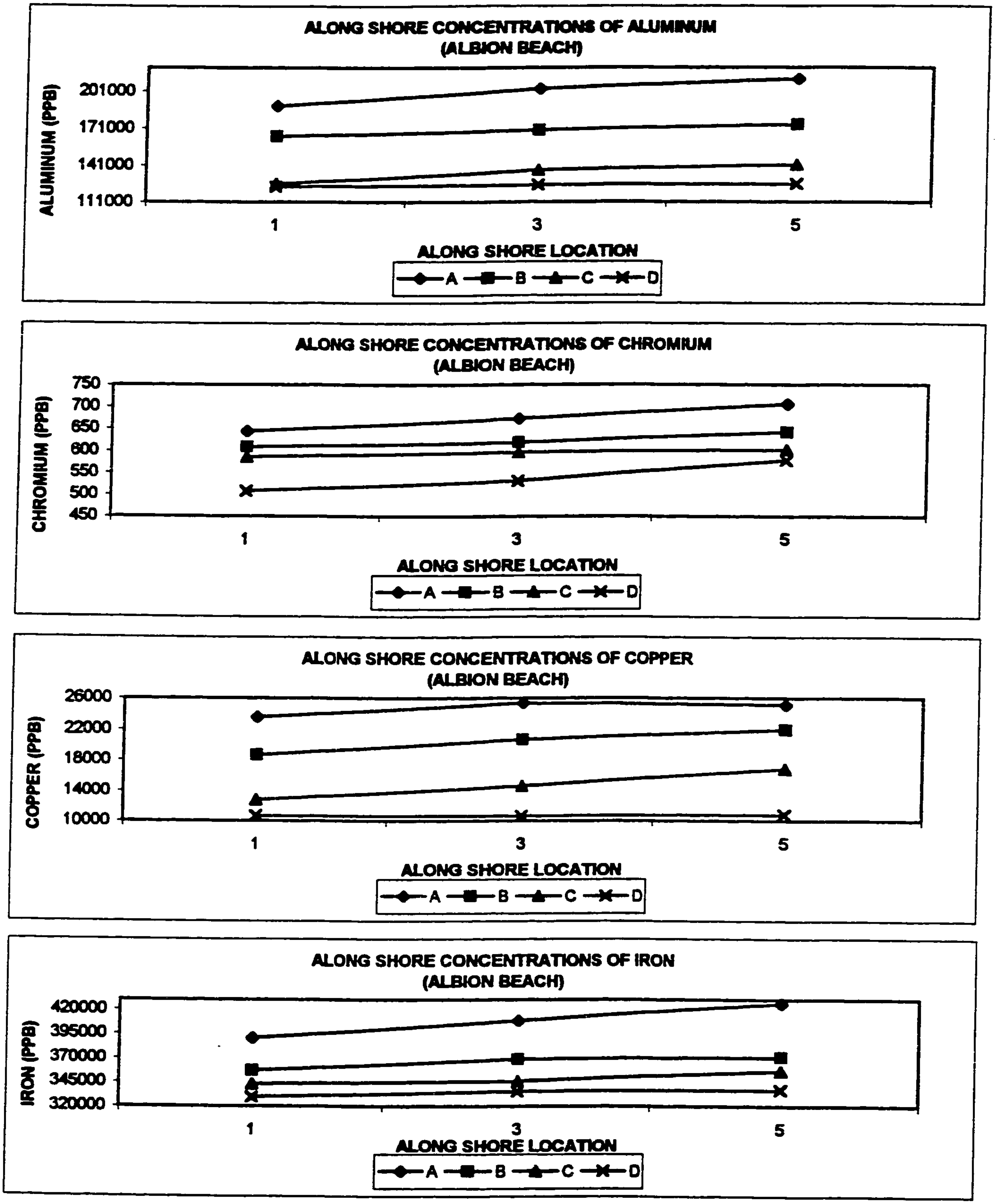
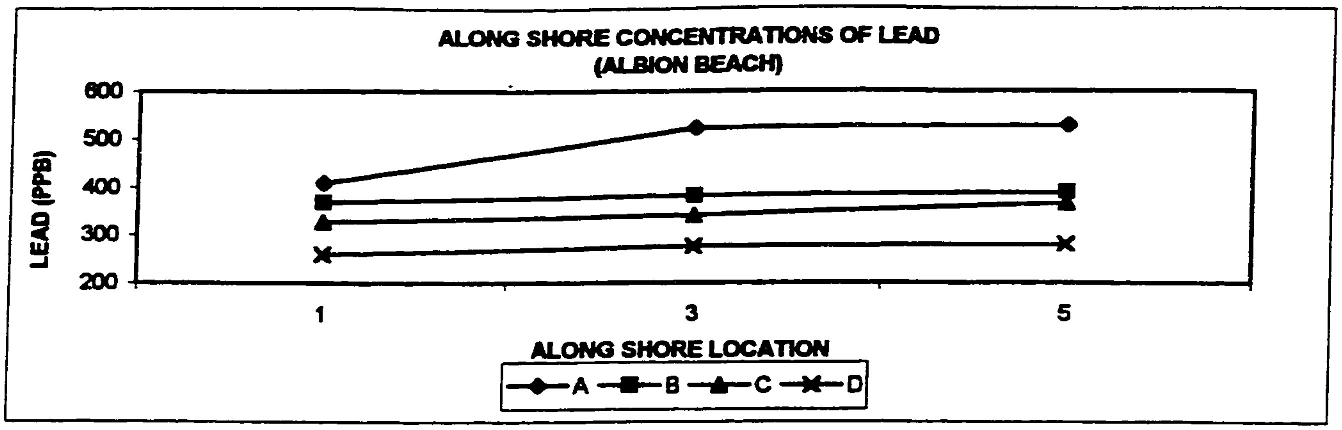
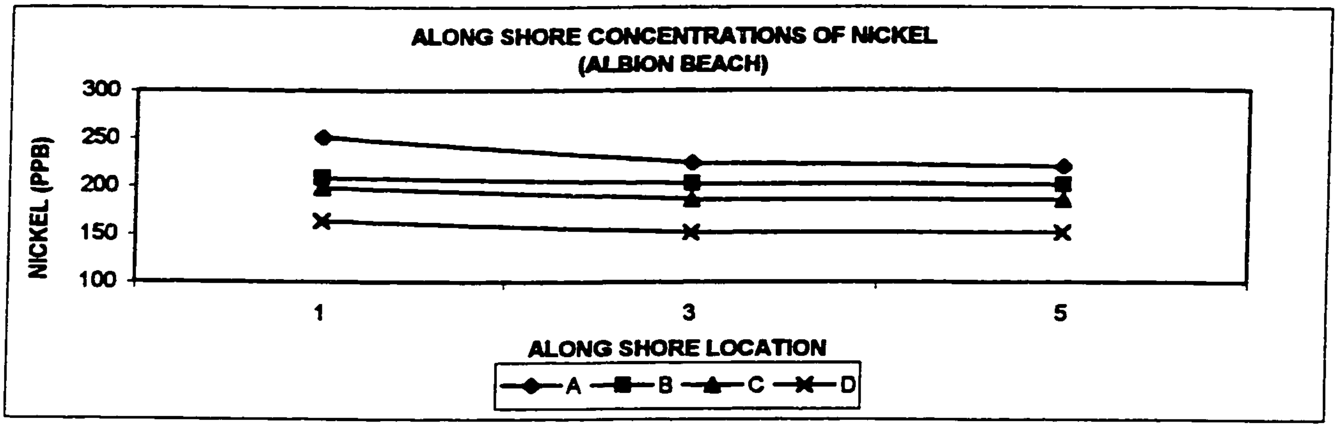
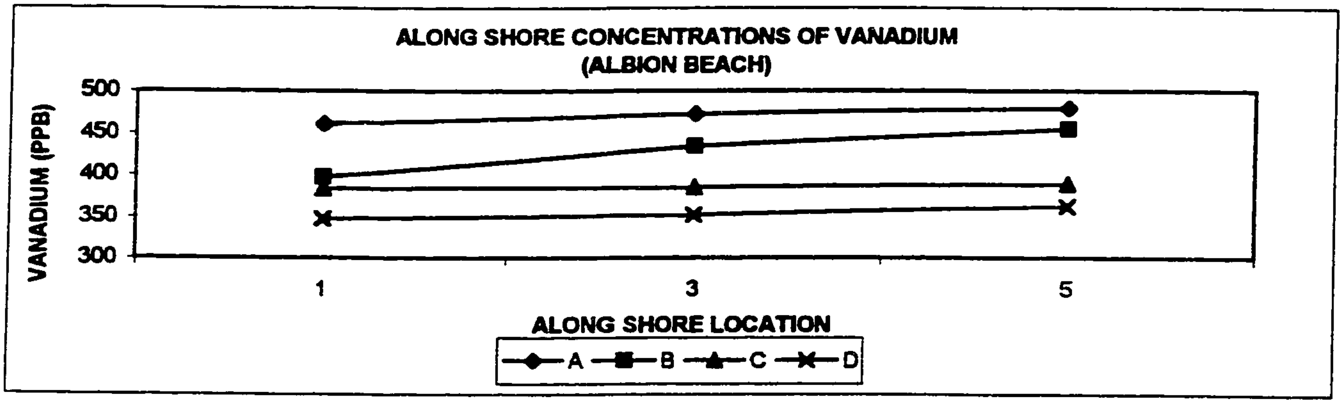

ACROSS SHORE CONCENTRATIONS OF ZINC
(MELANIE BEACH)
ZINC (PPB)
3600
3300
3000
2700
2400
2100
1800
A
B
C
D
ACROSS SHORE LOCATION
1
3
5

Figure 4.11: Along-Shore Concentrations of Heavy Metals (Albion Beach)




ALONG SHORE CONCENTRATIONS OF LEAD
(ALBION BEACH)
LEAD (PPB)
600
500
400
300
200
1
3
5
ALONG SHORE LOCATION
A B C D


ALONG SHORE CONCENTRATIONS OF NICKEL
(ALBION BEACH)
NICKEL (PPB)
300
250
200
150
100
1
3
5
ALONG SHORE LOCATION
A B C D


ALONG SHORE CONCENTRATIONS OF VANADIUM
(ALBION BEACH)
VANADIUM (PPB)
500
450
400
350
300
1
3
5
ALONG SHORE LOCATION
A B C D

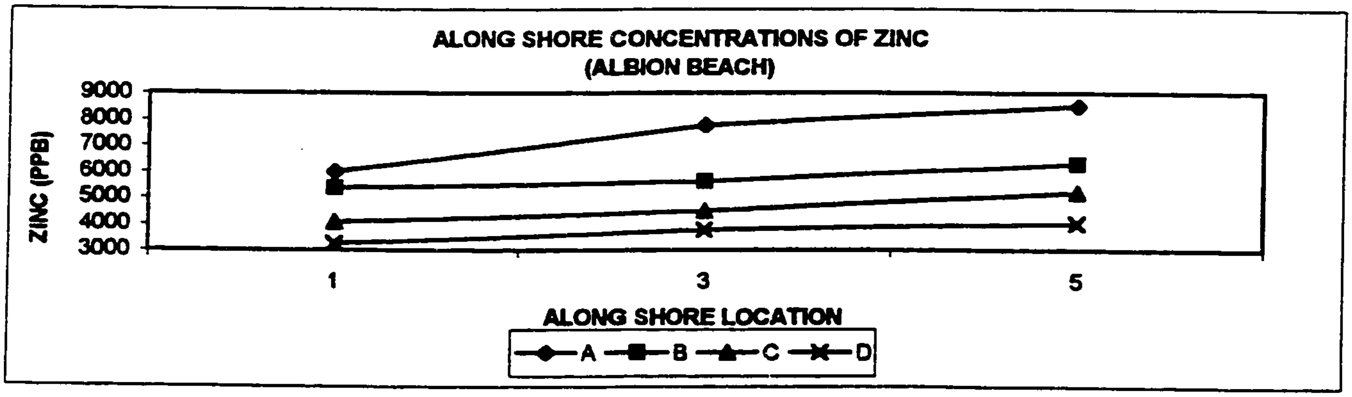
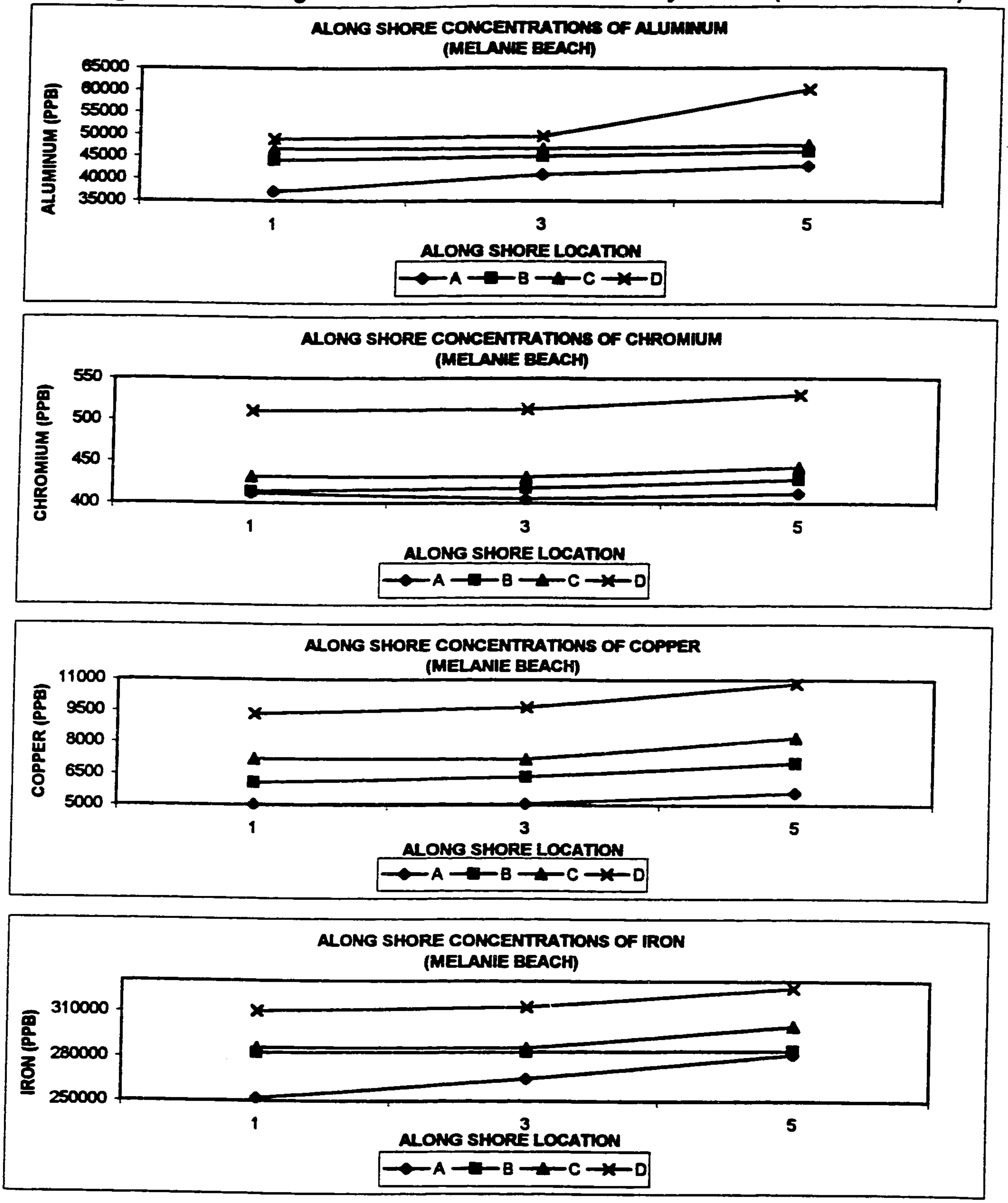
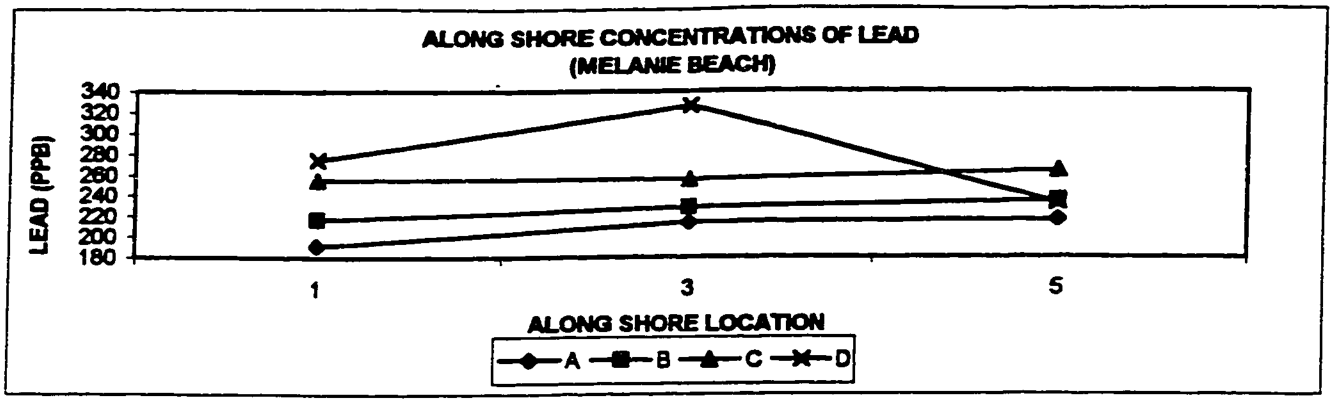
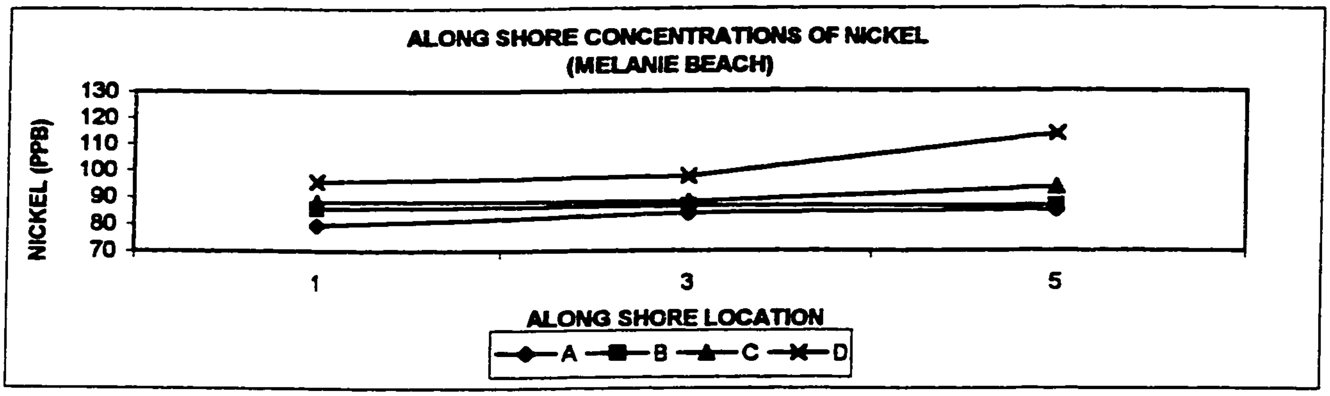
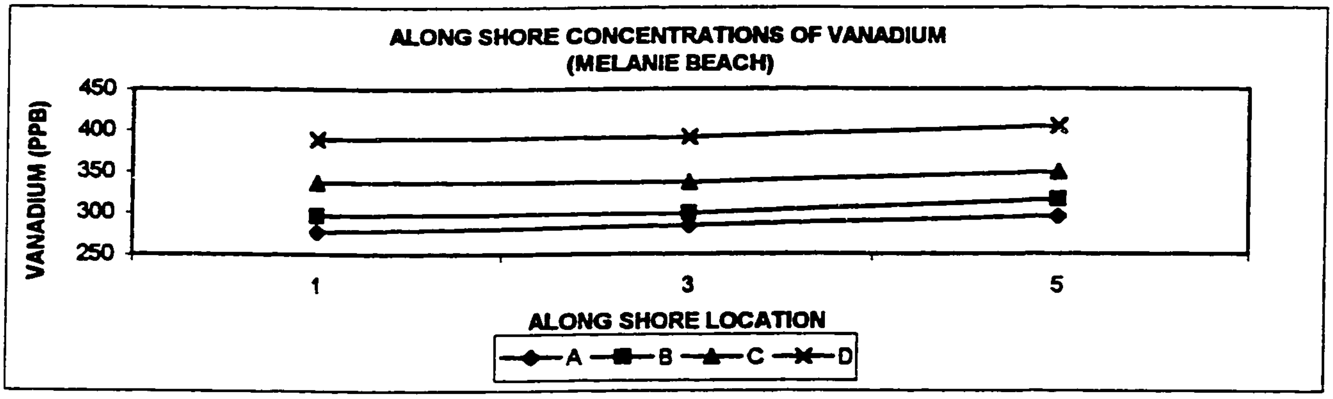

ALONG SHORE CONCENTRATIONS OF ZINC
(ALBION BEACH)
ZINC (PPB)
9000
8000
7000
6000
5000
4000
3000
1
3
5
ALONG SHORE LOCATION
A B C D

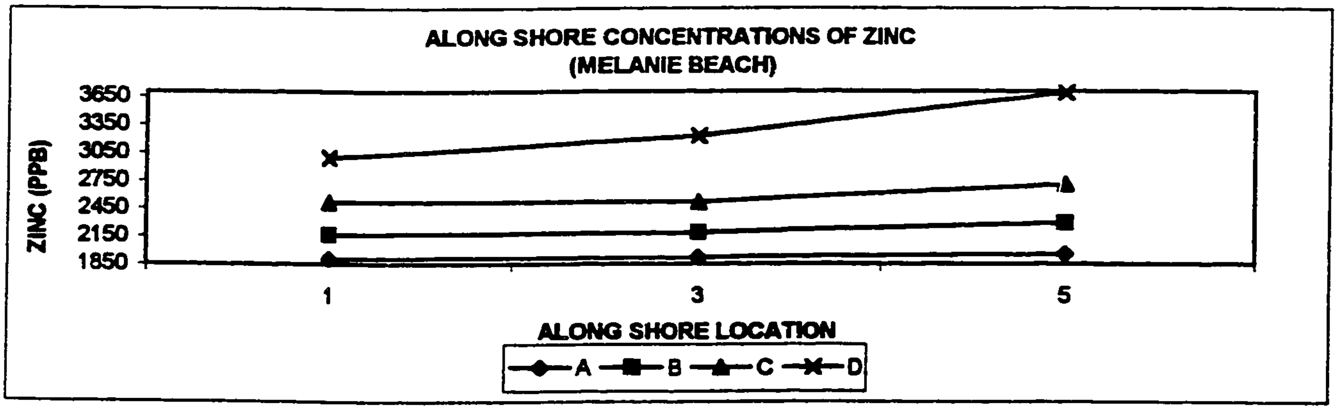
Figure 4.12: Along-Shore Concentrations of Heavy Metals (Melanie Beach)




ALONG SHORE CONCENTRATIONS OF LEAD
(MELANIE BEACH)
LEAD (PPB)
340
320
300
280
260
240
220
200
180
1
3
5
ALONG SHORE LOCATION
A
B
C
D


ALONG SHORE CONCENTRATIONS OF NICKEL
(MELANIE BEACH)
NICKEL (PPB)
130
120
110
100
90
80
70
1
3
5
ALONG SHORE LOCATION
A
B
C
D


ALONG SHORE CONCENTRATIONS OF VANADIUM
(MELANIE BEACH)
VANADIUM (PPB)
450
400
350
300
250
1
3
5
ALONG SHORE LOCATION
A
B
C
D


ALONG SHORE CONCENTRATIONS OF ZINC
(MELANIE BEACH)
ZINC (PPB)
3650
3350
3050
2750
2450
2150
1850
1
3
5
ALONG SHORE LOCATION
A
B
C
D

4.1.3 Analysis of Variance Results:

Analysis of variance was conducted to further investigate relationships between heavy metal concentrations and the variables beach state and sediment size. The results of the multiple or two-way analysis of variance will be presented first. With respect to the multiple analysis of variance, both beach state and sediment size were entered as independent variables while the natural logarithms of the heavy metal concentrations were entered as the dependent variable. The natural logarithms of the heavy metal concentrations were used to reduce heteroschedacity among the data.

The results of the multiple analysis of variance are presented in Table 4.1. Table 4.1 depicts a series of tests of between-subjects effects. The results of the general linear model (Table 4.1) reveal that the concentrations of each of the heavy metals under investigation differ significantly between the two beaches. In other words, significant variations in the concentrations of the heavy metals exist between the two beaches. That significant variations in the concentrations of heavy metals exist between the two beaches was previously established by the results of discriminant analysis. With the use of multiple analysis of variance, however, one is able to determine which of the independent variables and/or interactions between them account for the variations in the concentrations of heavy metals.

The results of the tests of between-subjects effects for the variable beach state (Table 4.1) indicate that beach state accounts for significant variations between the group means of the heavy metals aluminum, chromium and vanadium. With the exception of aluminum, beach state accounts for no more than 5% of the total variations in the corrected model for each heavy metal under study. The effects of beach state on the

Table 4.1: Multiple Analysis of Variance Results

Tests of Between-Subjects Effects

Source	Dependen Variable	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	LNAL	36.5950	5	7.319	269.2130	0.000
	LNCR	2.4740	5	0.549	79.6460	0.000
	LNCU	143.2760	5	28.665	1363.7350	0.000
	LNFE	4.6240	5	0.925	394.2390	0.000
	LNNI	33.0050	5	6.601	582.8920	0.000
	LNPB	96.7000	5	19.341	654.0080	0.000
	LNV	2.1800	5	0.436	75.1060	0.000
	LNZN	27.3660	5	5.473	225.1630	0.000
Beach State	LNAL	29.3700	1	0.000	1080.2970	0.000
	LNCR	0.0645	1	0.000	9.3530	0.003
	LNCU	0.0268	1	0.000	1.2790	0.262
	LNFE	0.0800	1	0.000	0.3410	0.561
	LNNI	0.0128	1	0.000	1.1310	0.291
	LNPB	0.0237	1	0.000	0.8020	0.374
	LNV	0.1270	1	0.000	21.8480	0.000
	LNZN	0.0417	1	0.000	1.7130	0.195
Sediment Size	LNAL	6.8720	2	0.000	126.3910	0.000
	LNCR	2.6640	2	0.000	193.1660	0.000
	LNCU	143.2480	2	0.000	3408.6630	0.000
	LNFE	4.6200	2	0.000	984.7220	0.000
	LNNI	32.9810	2	0.000	1456.1750	0.000
	LNPB	96.6610	2	0.000	1634.2910	0.000
	LNV	1.9040	2	0.000	164.0540	0.000
	LNZN	27.3150	2	0.000	561.8570	0.000
Beach State & Sediment Size	LNAL	0.3530	2	0.000	6.4930	0.003
	LNCR	0.0176	2	0.000	1.2720	0.287
	LNCU	0.0147	2	0.000	0.0350	0.966
	LNFE	0.0331	2	0.000	0.7050	0.498
	LNNI	0.0111	2	0.195	0.4890	0.615
	LNPB	0.0194	2	0.000	0.3290	0.721
	LNV	0.1480	2	0.195	12.7880	0.000
	LNZN	0.0937	2	0.000	0.1930	0.825

concentrations of these three heavy metals are further explored below. From Table 4.1 it is evident that from the results of the test of between-subjects effects for the variable sediment size that sediment size accounts for significant variations between the group means of all of the heavy metals under study. With the exception of aluminum, sediment size accounts for more than 90% of the total variations in the corrected model for each heavy metal under study. The effects of the interactions between the two independent variables, beach state and sediment size (Table 4.1), account for significant variations in the concentrations of two of the eight heavy metals. These heavy metals are aluminum and vanadium. Despite having significant effects on the variations in the concentrations of aluminum and vanadium, like the variable beach state, the interactions between beach state and sediment size have minimal effects (< 1%) on the total between beach variations for each metal within the corrected model.

To further explore the effects of beach state and the interactions between beach state and sediment size on the concentrations of aluminum, chromium and vanadium one-way analyses of variance were conducted for each beach (Table 4.2). For each beach, sediment size was entered as the independent variable and the natural logarithms of the concentrations of aluminum, chromium and vanadium were entered as the dependent variables.

The one-way analysis of variance eliminates the effects of beach state and the interaction effects between beach state and sediment size. Thus, comparisons between the three metals solely on the effects of sediment size could be made. From Table 4.2 it is evident that between group variations account for the majority of the total variations between the two beaches in the cases of aluminum, chromium and vanadium. On average,

Table 4.2: Analysis of Variance Results of Selected Heavy Metals for Albion and Melanie Beaches

ANOVA - Albion Beach

		Sum of Squares	df	Mean Square	F	Sig.
LNAL	Between Groups	2.108	2	1.054	26.758	0.000
	Within Groups	1.300	33	0.039		
	Total	3.408	35			
LNCR	Between Groups	1.209	2	0.604	93.402	0.000
	Within Groups	0.214	33	0.065		
	Total	1.422	35			
LNV	Between Groups	1.200	2	0.600	126.429	0.000
	Within Groups	0.157	33	0.047		
	Total	1.357	35			

ANOVA - Melanie Beach

		Sum of Squares	df	Mean Square	F	Sig.
LNAL	Between Groups	5.118	2	2.559	170.744	0.000
	Within Groups	0.495	33	0.015		
	Total	5.612	35			
LNCR	Between Groups	1.473	2	0.737	100.593	0.000
	Within Groups	0.242	33	0.073		
	Total	1.715	35			
LNV	Between Groups	0.852	2	0.043	62.122	0.000
	Within Groups	0.226	33	0.068		
	Total	1.079	35			

approximately 82% of the total variations among the concentrations of heavy metals between the two beaches are accounted for by between group variations. Of the total variations in the concentrations of heavy metals between the two beaches, Albion beach concentrations account for a larger percentage of the variations in the case of vanadium only.

4.1.4 Correlation and Regression Analysis Results:

The tests of between-subjects effects (Table 4.1) that conducted in the multiple analysis of variance revealed that the interactions between grain-size and heavy metal concentrations were statistically similar for both beaches in all cases except for the metals aluminum and vanadium. Since the interactions between grain-size and the heavy metal concentrations of aluminum and vanadium were significantly different for Albion and Melanie beach, separate executions of correlation and regression analysis were performed for each beach for these two metals only. In total, ten executions of correlation and regression analysis were performed. In all cases, the grain-size of sediment in Phi (ϕ) units was entered as the independent variable (X) and the natural logarithms of the heavy metal concentrations for each of the metals of concern were entered as the dependent variables (Y). The natural logarithms of the heavy metal concentrations were used to reduce heteroschedacity among the data. With respect to assessing the results of correlation and regression analysis, several statistics were of concern. Among these statistics were the Pearson correlation coefficient (r), the coefficient of determination (r^2), significance, the regression coefficient (b) and the regression intercept (a).

The Pearson correlation coefficient (r) relates the variance in the dependent variable (Y) to the reduction in that variance when the independent variable (X) is used to estimate values of Y. The Pearson correlation coefficient (r) indicates the strength of the relationship. The coefficient of determination (r^2) multiplied by 100% yields the percentage of variation in the dependent variable (Y) accounted for by variations in the independent variable (X). The regression coefficient (b) is a measure of the sensitivity of the dependent variable (Y) to changes in the independent variable (X). The direction of the relationship can be obtained from the sign in front of the regression coefficient. Lastly, the regression intercept (a) is represented by a value, which defines the point on the y axis of the scatter diagram that intersects with the regression line. The regression coefficient and the regression intercepts can be combined to form the quadratic regression equation which takes the form of $y = a +/- bx +/- bx^2$. Collectively, the statistics defined above will be used to describe each of the 10 relationships under investigation in terms of their strength, direction, sensitivity and significance.

Figure 4.13 depicts the results of the correlation and regression analysis between aluminum and grain-size for both Albion and Melanie beaches. The results of the correlation and regression analysis of aluminum versus sediment size for Albion beach will be presented first, followed by the results of Melanie beach. As evidenced by the Pearson correlation coefficient of 0.787, the relationship between the grain-size of sediment and the heavy metal aluminum for Albion beach is strong. Nearly 62 % of the variations in the concentration of aluminum are accounted for by variations in grain-size. Both the Pearson correlation coefficient and the coefficient of determination are statistically significant. Despite having a positive regression intercept (13.0652), this relationship is inverse. The reason for this is such that the Phi (ϕ) scale is an inverted scale. Essentially, the Phi (ϕ) scale behaves like and should be interpreted similar to that of a negative scale. The

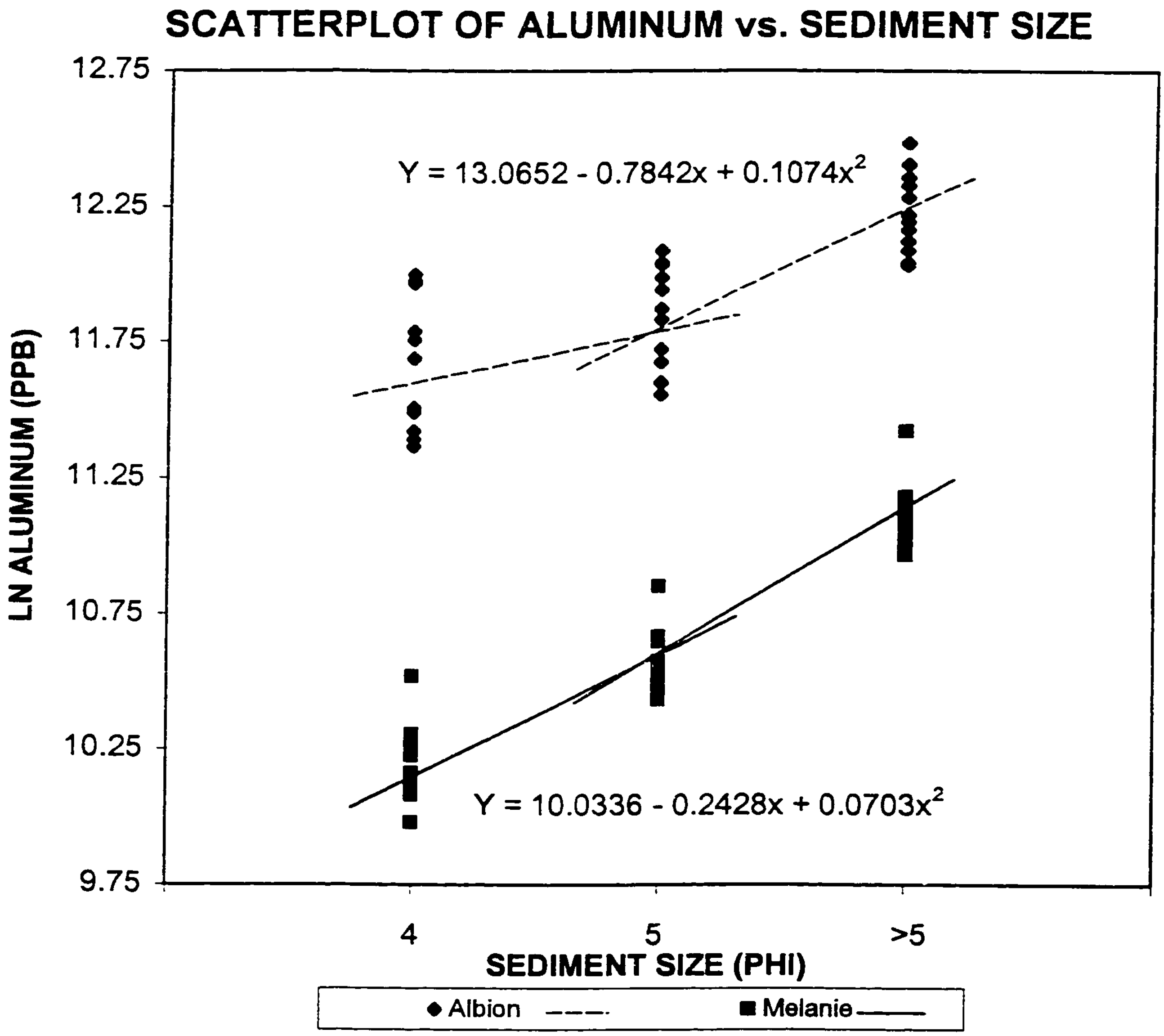
Figure 4.13 : Correlation and Regression Analysis Results for LN Aluminum (PPB) vs. Sediment Phi Groups (4,5,>5)

Model Summary

Model	Method	R	R Sqr	F	Sig. F	bO	b1	b2
Beach 1	QUA	0.787	0.619	49.23	0.000	13.0652	-0.7842	0.1074
Beach 2	QUA	0.955	0.912	170.74	0.000	10.0336	-0.2428	0.0703

a) Predictors: (Constant), SEDSIZE

b) Dependent Variables: LNALAL & LNALMEL



relationship is hypersensitive as indicated by the magnitude of the regression intercept (b_o = 13.0652). The quadratic regression equation is as follows: $y = 13.0652 - 0.7842x + 0.1074x^2$. The quadratic regression equation indicates an accelerating increase in aluminum concentrations with respect to particle size.

The results of the correlation and regression analysis between aluminum and grain-size for Melanie beach (Figure 4.13) are presented here. This relationship is very strong ($r = 0.955$). Approximately 91 % of the variations in the concentrations of aluminum are accounted for by variations in grain-size. Both the r and r^2 values are statistically significant. Moreover, the relationship is inverse and hypersensitive ($b_o = 10.0336$). For this particular relationship, the quadratic regression equation is as follows: $y = 10.0336 - 0.2428x + 0.0703x^2$, which describes an accelerating increase in aluminum concentrations with respect to declining particle sizes.

Figure 4.14 portrays the results of the correlation and regression analysis between chromium and grain-size. The strength of this relationship is considered to be strong ($r = 0.912$). Roughly 83 % of the variations in the concentrations of chromium are accounted for by variations in grain-size. The values of the correlation coefficient and the coefficient of determination are both statistically significant. In terms of direction, this relationship is inverse. Moreover, this relationship is hypersensitive ($b_o = 6.7276$). The quadratic regression equation is as follows: $y = 6.7276 - 0.4528x + 0.0685x^2$. As evidenced by the regression equation, the rate of heavy metal increase, accelerates with declining particle size.

The relationship between the heavy metal copper and grain-size (Figure 4.15) is best described as being extremely strong ($r = 0.995$), statistically significant (0.000),

Figure 4.14 : Correlation and Regression Analysis Results for LN Chromium (PPB) vs. Sediment Phi Groups (4,5,>5)

Model Summary

Model	Method	R	R Sqr	F	Sig. F	bO	b1	b2
Beach	QUA	0.912	0.832	171.1	0.000	6.7276	-0.4528	0.0685

a) Predictors: (Constant), SEDSIZE
b) Dependent Variables: LNCR

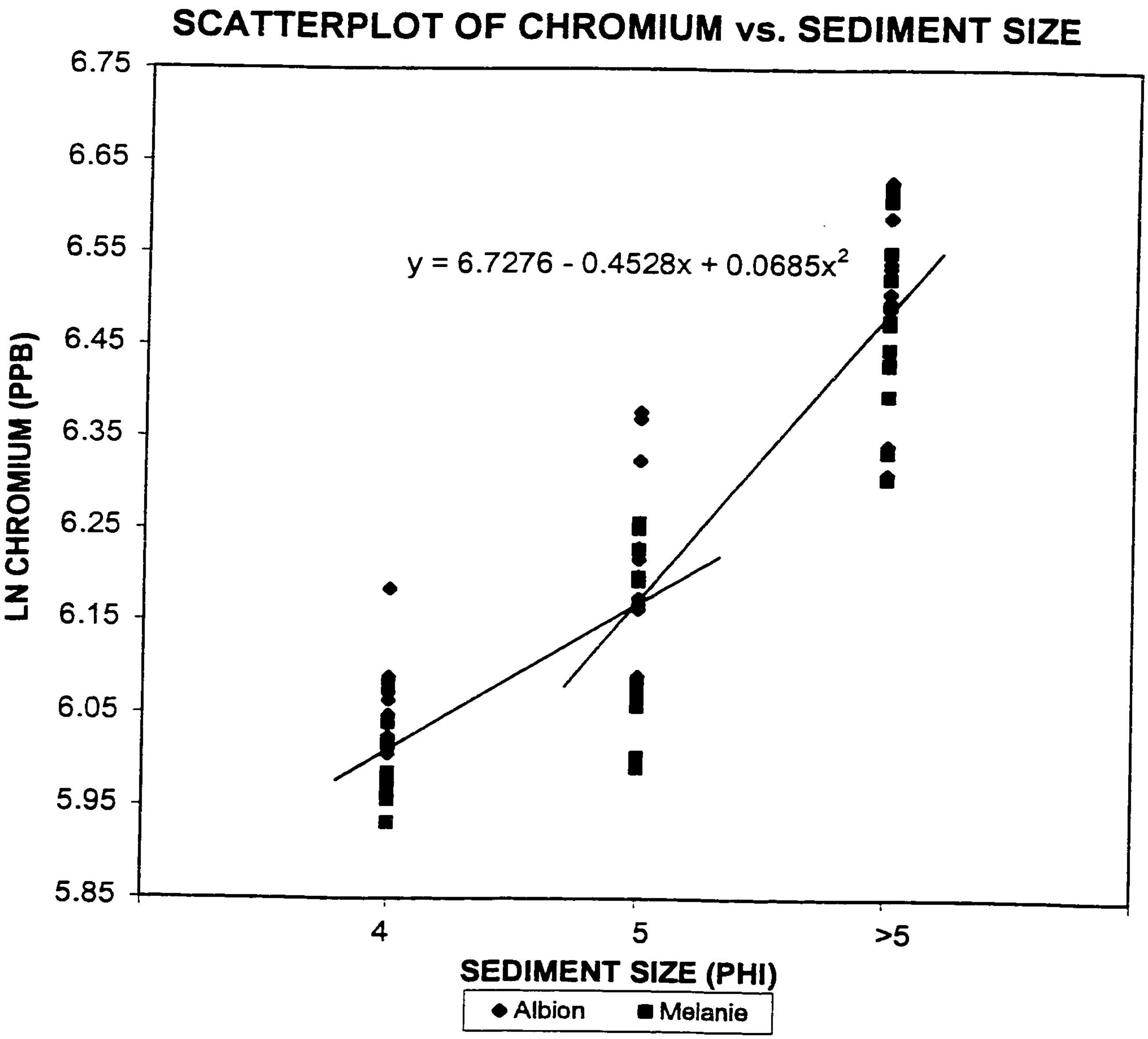


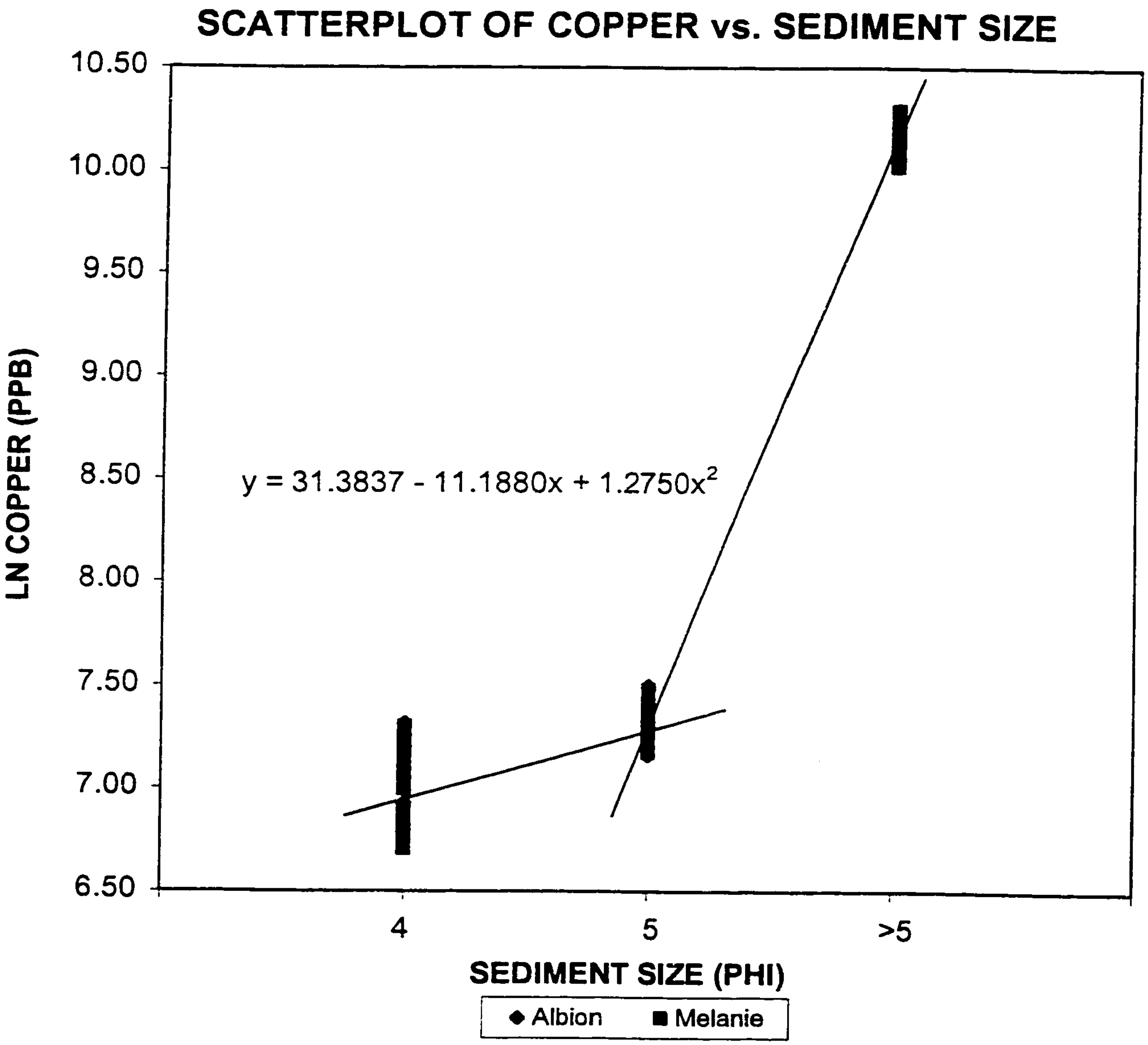
Figure 4.15 : Correlation and Regression Analysis Results for LN Copper (PPB) vs. Sediment Phi Groups (4,5,>5)

Model Summary

Model	Method	R	R Sqr	F	Sig. F	bO	b1	b2
Beach	QUA	0.995	0.99	3492.2	0.000	31.3837	-11.188	1.2750

a) Predictors: (Constant), SEDSIZE

b) Dependent Variables: LNCU



inverse as well as hypersensitive ($b_o = 31.3837$). Moreover, in round numbers, 99 % of the variations in the concentrations of copper are accounted for by variations in grain-size. A quadratic regression equation of $y = 31.3837 - 11.1880x + 1.2750x^2$ was obtained from the regression execution indicating that the relationship between copper and grain-size accelerates at an increasing rate with decreasing particle size.

The results of the correlation and regression analysis for the relationship between the heavy metal iron and grain-size can be seen in Figure 4.16. In terms of strength, this relationship is best described as being very strong ($r = 0.983$). Just over 96 % of the variations in the concentrations of iron can be accounted for by variations in grain-size. The results of the correlation and regression analysis are statistically significant. This relationship as indicated by the regression intercept ($b_o = 15.2980$) is inverse as well as hypersensitive to changes in either iron concentrations or grain-size. The quadratic regression equation is $y = 15.2980 - 1.4120x + 0.1706x^2$. The positive term in front of the second regression coefficient indicates that the relationship between iron and grain-size accelerates with decreasing particle size.

Figure 4.17 portrays the results of the correlation and regression execution between the heavy metal nickel and grain-size. The relationship between nickel and grain-size is very strong ($r = 0.988$), statistically significant, inverse and sensitive ($b_o = 3.0793$). Nearly, 98 % of the variations in nickel concentrations can be accounted for by variations in grain-size. The quadratic regression equation that describes this relationship is $y = 3.0793 + 2.3581x - 0.1534x^2$. The negative term in front of the second regression coefficient indicates that the relationship between nickel and grain-size increases at a decelerating rate with decreasing particle size.

Figure 4.16 : Correlation and Regression Analysis Results for LN Iron (PPB) vs. Sediment Phi Groups (4,5,>5)

Model Summary

Model	Method	R	R Sqr	F	Sig. F	bO	b1	b2
Beach	QUA	0.983	0.967	1002.9	0.000	15.298	-1.4120	0.1706

a) Predictors: (Constant), SEDSIZE

b) Dependent Variables: LNFE

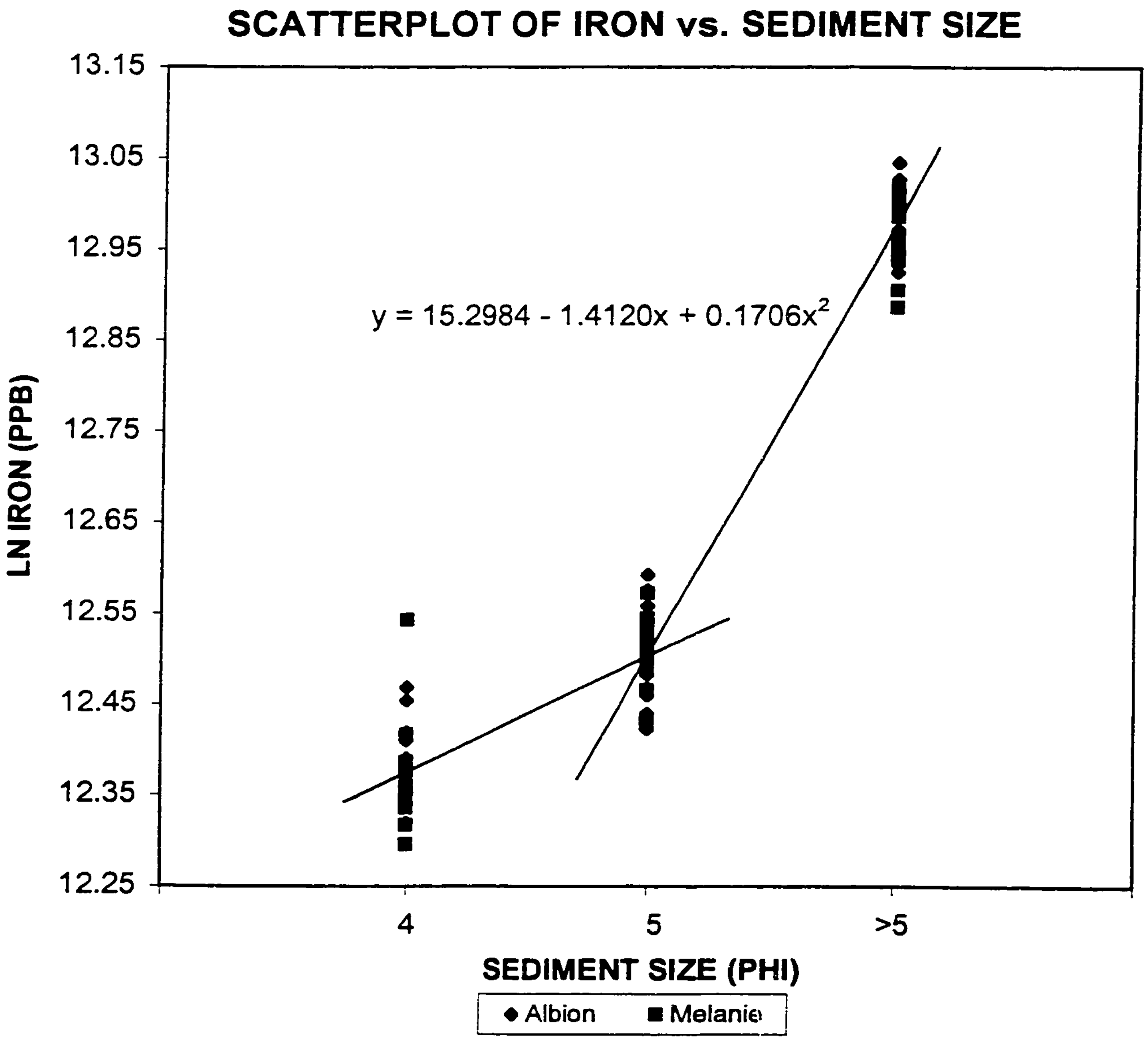
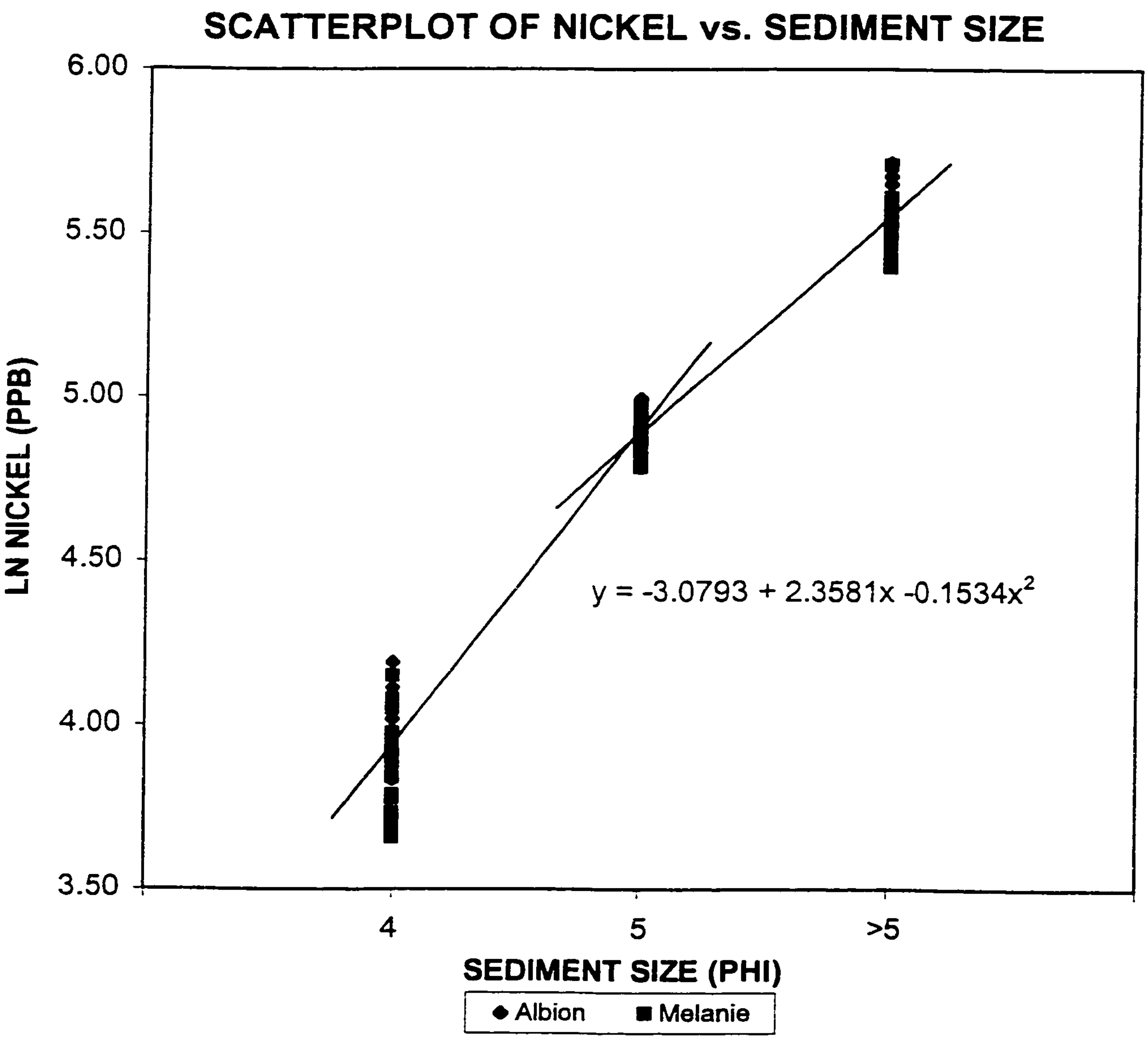


Figure 4.17 : Correlation and Regression Analysis Results for LN Nickel (PPB) vs. Sediment Phi Groups (4,5,>5)

Model Summary

Model	Method	R	R Sqr	F	Sig. F	bO	b1	b2
Beach	QUA	0.988	0.977	1475.2	0.000	-3.0793	2.3581	-0.1534

a) Predictors: (Constant), SEDSIZE
b) Dependent Variables: LNNI



The correlation and regression analysis results between lead and grain-size can be viewed in Figure 4.18. This relationship is also very strong ($r = 0.990$). Approximately 98 % of the variation in the concentrations of vanadium are accounted for by variations in grain-size. Both the r and r^2 values are statistically significant. This relationship is inverse as well as hypersensitive ($b_o = 9.6820$). The quadratic regression equation is as follows: $y = 9.6820 - 3.2840x + 0.4677x^2$. Lead concentrations increase at an accelerating rate with respect to decreasing grain-size.

The results of the correlation and regression execution for Albion beach (vanadium versus grain-size) are depicted in Figure 4.19. This relationship is best described as being strong ($r = 0.941$), statistically significant (0.000), inverse and sensitive ($b_o = 3.0404$). Approximately 89 % of the variations in vanadium concentrations for Albion beach can be accounted for by variations in grain-size. The quadratic regression equation is $y = 3.0404 + 0.9426x - 0.0723x^2$.

The results of the correlation and regression execution for Melanie beach (vanadium versus grain-size) are also depicted in Figure 4.19. As evidenced by the Pearson correlation coefficient of 0.889, the relationship between the heavy metal vanadium and grain-size is strong. Approximately 79 % of the variations in the concentrations of vanadium for Melanie beach are accounted for by variations in grain-size. Both the Pearson correlation coefficient and the coefficient of determination are statistically significant. The direction of the relationship is inverse. The quadratic regression equation is as follows: $y = 7.5125 - 0.8860x + 0.1064x^2$ which describes accelerating increases in vanadium concentrations with decreases in particle size.

Figure 4.18 : Correlation and Regression Analysis Results for LN Lead (PPB) vs. Sediment Phi Groups (4,5,>5)

Model Summary

Model	Method	R	R Sqr	F	Sig. F	bO	b1	b2
Beach	QUA	0.990	0.98	1671.6	0.000	9.682	-3.2840	0.4677

a) Predictors: (Constant), SEDSIZE

b) Dependent Variables: LNPB

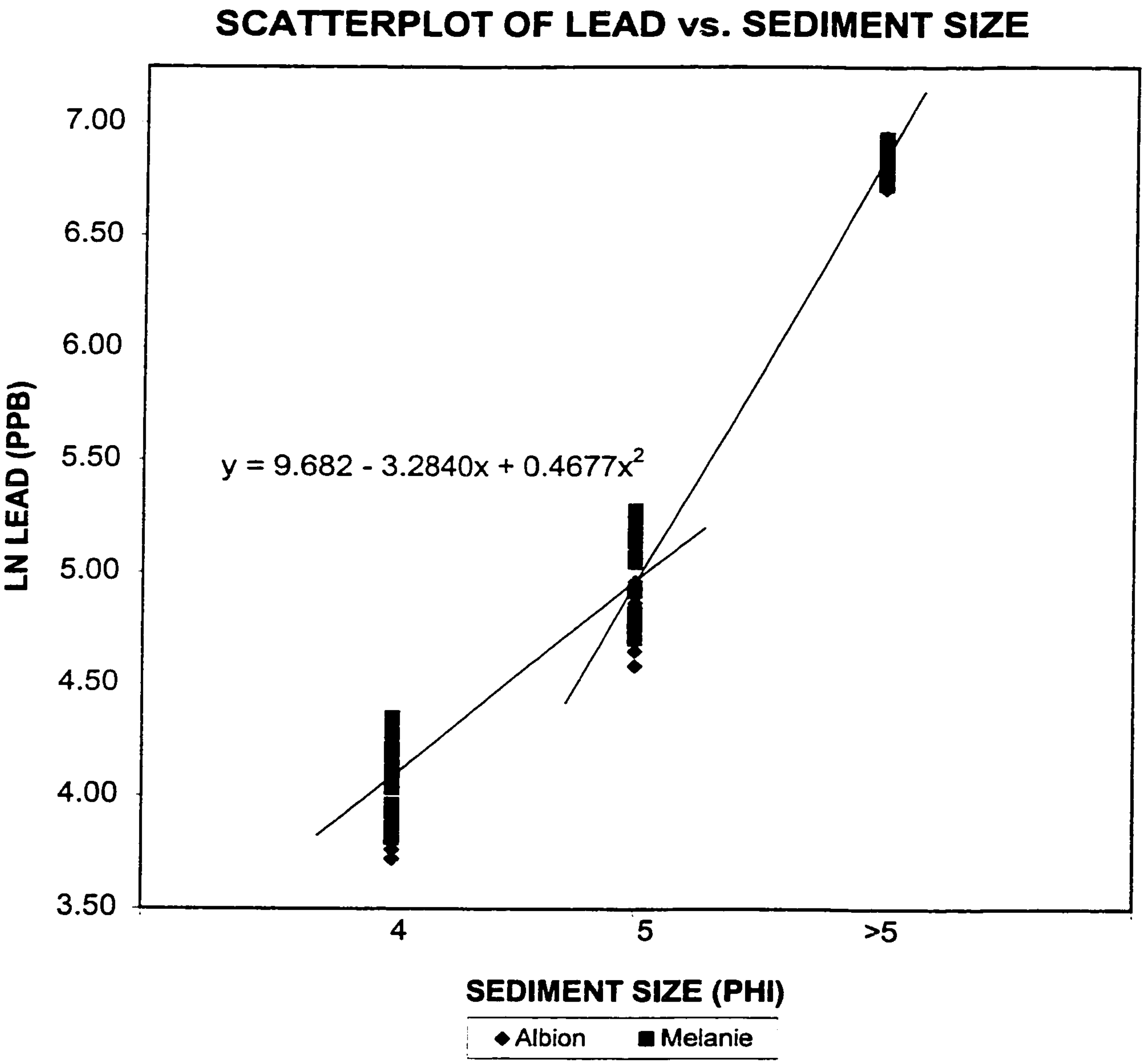
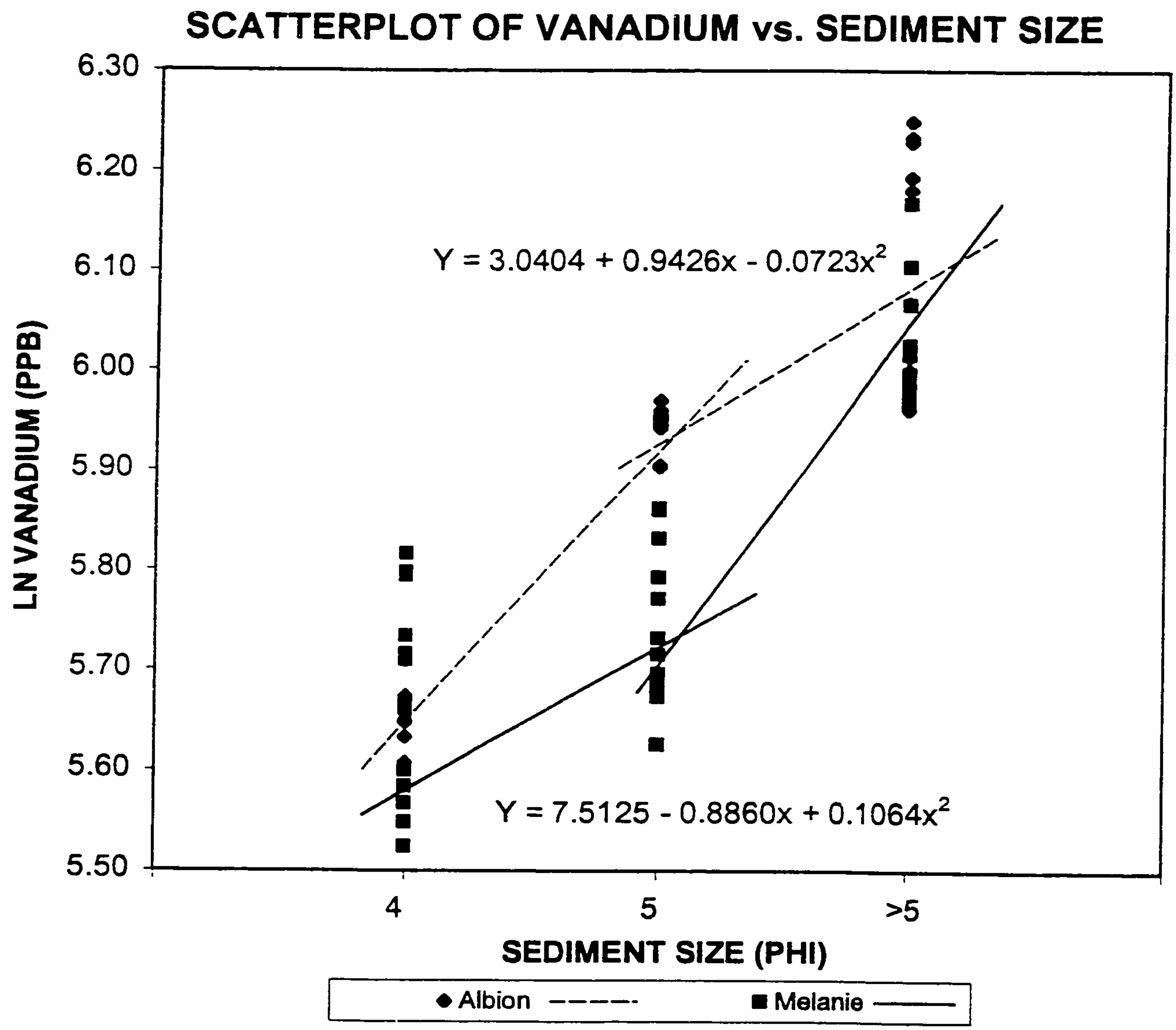


Figure 4.19 : Correlation and Regression Analysis Results for LN Vanadium (PPB) vs. Sediment Phi Groups (4,5,>5)

Model Summary

Model	Method	R	R Sqr	F	Sig. F	bO	b1	b2
Beach 1	QUA	0.941	0.885	126.43	0.000	3.0404	0.9426	-0.0723
Beach 2	QUA	0.889	0.790	62.12	0.000	7.5125	-0.886	0.1064

a) Predictors: (Constant), SEDSIZE
b) Dependent Variables: LNVAL & LNVMEL



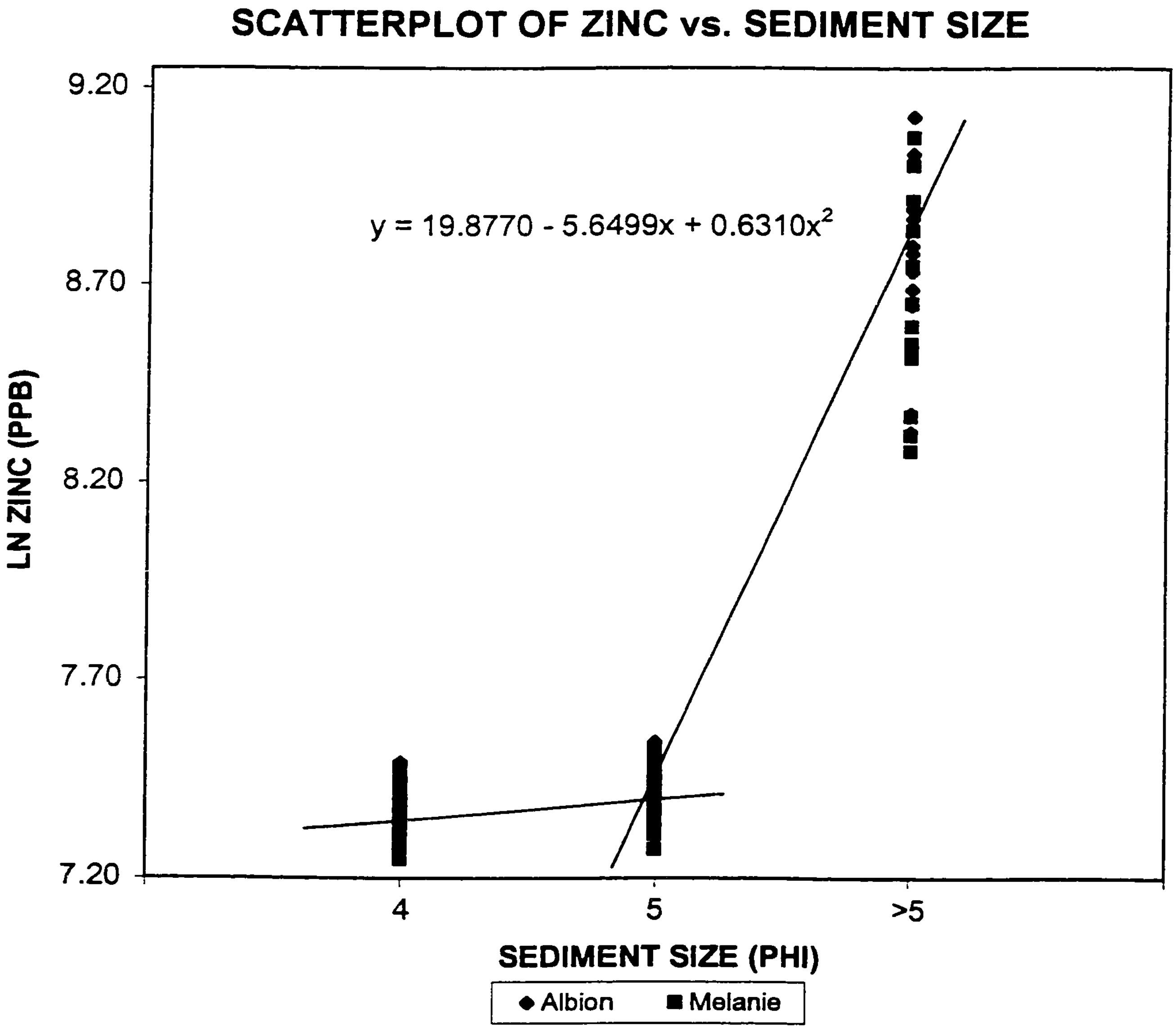
The results of the correlation and regression analysis between the heavy metal zinc and grain-size are displayed in Figure 4.20. From Figure 4.20 it is evident that this relationship is very strong ($r = 0.971$), statistically significant (0.000), inverse and hypersensitive ($b_o = 19.8770$). Furthermore, 94.3 % of the variations in the concentration of zinc can be accounted for by variations in grain-size. The quadratic regression equation derived from the regression analysis is $y = 19.8770 - 5.6499x + 0.6310x^2$. The quadratic regression equation depicts a relationship such that there is an acceleration in the increase of zinc with respect to decreasing grain-size.

Figure 4.20 : Correlation and Regression Analysis Results for LN Zinc (PPB) vs. Sediment Phi Groups (4,5,>5)

Model Summary

Model	Method	R	R Sqr	F	Sig. F	bO	b1	b2
Beach	QUA	0.971	0.943	569.29	0.000	19.8770	-5.6499	0.6310

a) Predictors: (Constant), SEDSIZE
b) Dependent Variables: LNZ



CHAPTER 5

5.1 Discussion:

An extensive review of the literature pertaining to the spatial distribution of heavy metals in coastal environments (for example, those studies conducted by De Gregori *et al.* (1996), Chakrapani and Subramanian (1993), Arakel and Hongjun (1992), Biksham *et al.* (1992), Wayne and Waters (1988), and Abernathy *et al.* (1984)) facilitated the development of two hypotheses. These hypotheses were formulated in such a manner that determining whether spatial variations in the concentrations of heavy metals exist between accreting and eroding beaches as well as within both beach types became the central focus of this thesis. The data collected in the field were statistically assessed in order to allow the hypotheses to be evaluated. This discussion will focus on determining whether the results of the statistical analyses warrant accepting or rejecting either of the two hypotheses. Once accepted or rejected, inferences will be advanced. Theories will be utilized, where possible, to support these inferences.

The first hypothesis that was advanced was that accreting beaches, with smaller grain-sizes and eroding beaches, with coarser grain-sizes will exhibit contrasting concentrations of heavy metals. The employment of discriminant analysis proved useful in assessing this hypothesis. From the eight executions of discriminant analysis (Figures 4.1-4.8) it is evident that for each metal under investigation that a high degree of between beach variations existed (canonical correlation = 0.929-0.638) while a far lower degree of within beach variations existed (Wilk's Lambda = 0.593-0.138). Furthermore, the results of all eight executions of discriminant analysis are statistically significant.

The utilization of analysis of variance also proved useful in assessing the first hypothesis. The tests of between subject effects from the multiple analysis of variance revealed that significant variations in the concentrations of each of the eight heavy metals under investigation exist between the two beach types. Based on the results of the eight executions of discriminant analysis as well the results of the multiple analysis of variance, the first hypothesis is accepted and it is inferred that accreting beaches, with smaller grain-sizes and eroding beaches, with coarser grain-sizes exhibit contrasting concentrations of heavy metals.

While discriminant analysis proved to be useful in allowing the above inferences to be made, its use failed to provide information as to why the differences in heavy metal concentrations exist. One must recall that the hypothesis that accreting beaches, with smaller grain-sizes and eroding beaches, with coarser grain-sizes exhibit contrasting concentrations of heavy metals was made based on the premise that grain-size was the controlling factor. To determine the likelihood that grain-size is in fact the controlling variable in the relationship inferred above, the results of the multiple analysis of variance were revisited and correlation and regression analysis were performed.

The results of the multiple analysis of variance can be re-examined in Table 4.1. From the tests of the between subjects effects (Table 4.1) it is evident that among the variables entered into the model that sediment size accounts for the majority of variations in the concentrations of heavy metals between the two beach types. With the exception of aluminum, approximately 90 % of the variations in the concentrations of heavy metals between the two beaches can be accounted for by variations in the grain-size of sediment. The effects of beach type and the interactions between beach type and sediment size accounted for a lesser and often insignificant proportion of the total variations in the concentrations of heavy metals between the two beaches.

The results of the ten executions of correlation and regression analysis performed in this investigation can be reviewed in Figures 4.13-4.20. The results of the executions of correlation and regression analysis reveal that a significantly strong relationship exists between the concentrations of the eight heavy metals under investigation and the grain-size of sediment from both beach types. This is evidenced by the Pearson correlation coefficients which range in magnitude from 0.995-0.787. Moreover, the findings suggest that between 61 and 99 % of the variations in the concentrations of heavy metals can be attributed to variations in the grain-size of sediment. The relationship between heavy metal concentrations and grain-size is also inverse. This inverse relationship indicates that as the grain-size of sediment decreases the concentrations of heavy metals increases or vice versa.

Evidently, the premise that variations in the concentrations of the eight heavy metals under investigation are attributed primarily to the grain-size of sediment is highly plausible. This finding is consistent with the findings of De Gregori *et al.* (1996), Maurer *et al.* (1994), Chakrapani and Subramanian (1993), Van Hattum *et al.* (1993) and Thompson *et al.* (1984). In addition to lending support to the inference advanced above, the results of the analysis of variance and the correlation and regression analysis are supported by as well as corroborate the theory that higher surface area-to-grain-size ratios characteristic of sediments smaller in size serve as the foundation for increased adsorption of heavy metals.

The second hypothesis that was advanced was that spatial variations in the concentrations of heavy metals are discernible and distinct in both across-shore and along-shore directions (westward) within accreting and eroding beaches. This hypothesis was also formulated on the basis that the grain-size of sediment is the controlling variable. The results of two separate series of line graphs (Figures 4.9 and 4.10) effectively established a foundation upon which the second hypothesis could be assessed.

From Figure 4.9 and Appendix Table 5 it is evident that distinct across-shore spatial variations in the concentrations of the eight heavy metals under investigation exist. More specifically, the concentrations of the eight heavy metals under investigation increase in a shoreward direction in each of the 24 cases for Albion beach while increasing in a seaward direction in each of the 24 cases for Melanie beach. When compared to the raw grain-size data (Appendix Table 1), it is apparent that the direction of heavy metal increase is opposite to that of the direction of grain-size increase. These results are consistent with those of the correlation and regression analysis. That is, an inverse relationship between heavy metal concentrations and the grain-size of sediment exists.

Distinct along-shore spatial variations in the concentrations of the eight heavy metals under investigation are apparent from Figure 4.10 and Appendix Table 6. An assessment of Figure 4.10 and Appendix Table 6 reveals that heavy metal concentrations increase in an east to west direction in 27 of 32 cases within Albion beach and in 26 of 32 cases within Melanie beach. The tendency for heavy metal concentrations to increase in an east to west direction within both beach types is opposite to that of the direction of grain-size increase (Appendix Table 1). These results are also consistent with the results of the correlation and regression analysis. In both cases, an inverse relationship between heavy metal concentrations and the grain-size of sediment is discernible.

Based on the results of the two separate series of line graphs as well as the heavy metal concentration data, the second hypothesis advanced in this thesis is accepted and it is inferred that spatial variations in the concentrations of heavy metals are discernible and distinct in both across-shore and along-shore directions (westward) within accreting and eroding beaches. Moreover, the premise that the spatial variations in the grain-size of sediment is the controlling factor in the above distributions is well supported by the grain-size data as well as the results of the multiple analysis of variance and the correlation and regression analysis.

Both of the hypotheses under investigation were made as well as assessed based on the notion that the grain-size of sediment was the dominant controlling factor with respect to the spatial distribution of heavy metals. The use of discriminant analysis in conjunction with line graphs and especially analysis of variance and correlation and regression analysis significantly support the premise that the grain-size of sediment is a dominant controlling variable in terms of the spatial distribution of heavy metals. With overwhelming support for this inference having been conjured from the analysis, the question as to why or how with the use of a restrictive grain-size fraction, a tool which has been used to circumvent the effects of grain-size bias in heavy metal analysis, can this support have been ascertained.

In order to provide a reasonable explanation for the restrictive grain-size fraction's inability to adequately circumvent the effects of grain-size, the raw grain-size data as well as the heavy metal data will be further examined. An assessment of Appendix Table 1 reveals that the two beaches are extremely different in terms of their sediment composition. The 100 g sample for Albion beach typically contains sediments which are much smaller than those of a 100 g sample for Melanie beach. While this is true, the 4, 5, and > 5 phi groups must be examined to gain insight into the inability of the restrictive grain-size fraction to eliminate the effects of grain-size on the spatial distribution of heavy metals. The typical 1 g sample for Albion beach that was submitted to GLIER for heavy metal analysis was comprised of 24 % 4 phi sediments, 32 % 5 phi sediments and 44 % > 5 phi sediments while the typical 1 g sample for Melanie beach was comprised of 32 % 4 phi sediments, 40 % 5 phi sediments and 27 % > 5 phi sediments. Evidently, the sediment distribution within the restrictive grain-size fraction is varied between the two beaches. The sediment distribution for Albion beach within the restrictive grain-size fraction is such that the majority of sediments are concentrated in the 5 and > 5 phi groups, Conversely, the majority of sediments within the restrictive grain-size fraction for Melanie beach are concentrated within the 4 and 5 phi groups. The assessment of the sediment distributions within the restrictive grain-size fraction demonstrates that the 1 g samples submitted for heavy metal analysis are in fact very different. It is apparent that the use of a restrictive grain-size fraction reduced the differences in grain-size between the two beaches but did not entirely eliminate those effects.

Tables 5.1 and 5.2 depict the differences in the concentrations of heavy metals between the 4, 5 and > 5 phi groups for each sampling location for Albion beach and Melanie beach respectively. Using the 4 phi group as a reference, values showing the number of times by which the 5 and > 5 phi group concentrations exceeded those of the 4

Table 5.1: Rate of Heavy Metal Concentration Increase by Phi Group (Albion Beach)

	Al	Cr	Cu	Fe	Ni	Pb	V	Zn
AL-1A-4 PHI	156991	430.4	1420	247070	66.2	67.7	286.2	1637
AL-1A-5 PHI	1.08	1.30	1.25	1.15	2.23	2.52	1.35	1.05
AL-1A>5PHI	1.48	1.61	20.06	1.84	4.59	14.03	1.77	4.43
AL-1B-4 PHI	119121	412.2	1205	240627	53.8	51.7	279.5	1640
AL-IB-5 PHI	1.20	1.19	1.34	1.11	2.45	2.76	1.38	1.01
AL-1B>5 PHI	1.71	1.61	21.75	1.79	5.05	17.43	1.84	3.97
AL-1C-4 PHI	91327	406.1	1021	234621	48.7	47.5	270.8	1571
AL-IC-5 PHI	1.29	1.81	1.69	1.10	2.66	2.58	1.41	1.02
AL-1C>5 PHI	2.01	1.62	24.29	1.78	5.20	18.02	1.46	3.63
AL-1D-4 PHI	86246	388.2	856	224063	41.6	41.4	272.4	1500
AL-ID-5 PHI	1.21	1.14	1.51	1.11	3.01	2.36	1.34	1.02
AL-1D>5 PHI	1.95	1.41	27.41	1.83	6.00	19.83	1.42	2.76
AL-3A-4 PHI	158290	433.9	1507	256458	61.3	70.4	288.3	1727
AL-3A-5 PHI	1.07	1.35	1.19	1.13	2.29	2.63	1.34	1.02
AL-3A>5 PHI	1.54	1.69	19.68	1.75	4.76	14.50	1.77	4.84
AL-3B-4 PHI	127631	419.3	1293	245377	49.9	56.8	283.7	1653
AL-3B-5 PHI	1.20	1.20	1.28	1.12	2.38	2.76	1.35	1.03
AL-3B>5 PHI	1.69	1.60	21.10	1.79	5.33	16.20	1.71	4.01
AL-3C-4 PHI	97663	408.4	1089	232294	48.1	49.3	290	1577
AL-3C-5 PHI	1.26	1.20	1.36	1.19	2.67	2.63	1.32	1.02
AL-3C>5 PHI	1.96	1.61	23.24	1.81	5.27	17.60	1.41	3.76
AL-3D-4 PHI	91304	393.7	897	228846	43.8	44.8	284.3	1527
AL-3D-5 PHI	1.20	1.21	1.45	1.09	2.74	2.32	1.29	1.03
AL-3D>5 PHI	1.85	1.45	25.90	1.81	5.52	18.59	1.40	2.84
AL-5A-4 PHI	162310	441	1487	260065	55.7	73.9	290.6	1794
AL-5A-5 PHI	1.09	1.33	1.21	1.13	2.51	2.59	1.35	1.05
AL-5A>5 PHI	1.63	1.71	19.95	1.79	5.10	13.95	1.78	2.84
AL-5B-4 PHI	131440	423.6	1346	247642	50.5	60.2	288.1	1711
AL-5B-5 PHI	1.22	1.20	1.26	1.10	2.59	2.70	1.33	1.05
AL-5B>5 PHI	1.72	1.60	20.80	1.79	5.11	15.60	1.70	5.13
AL-5C-4 PHI	99404	413.6	1155	238082	46.3	52.6	301.7	1608
AL-5C-5 PHI	1.44	1.18	1.37	1.11	2.67	2.63	1.30	1.02
AL-5C>5 PHI	1.98	1.60	22.46	1.80	5.44	19.00	1.37	4.18
AL-5D-4 PHI	88506	485.1	914	231479	41.5	43.1	291.1	1546
AL-5D-5 PHI	1.23	0.98	1.32	1.09	2.93	2.72	1.32	1.03
AL-5D>5 PHI	2.01	1.28	25.40	1.79	5.87	19.23	1.88	3.86

Table 5.2: Rate of Heavy Metal Concentration Increase by Phi Group (Melanie Beach)

	Al	Cr	Cu	Fe	Ni	Pb	V	Zn
MEL-1A-4 PHI	21632	388.7	818	218764	38.8	46.2	250.8	1405
MEL-1A-5 PHI	1.58	1.03	1.62	1.15	3.08	2.43	1.11	1.03
MEL-1A>5 PHI	2.68	1.41	27.41	1.80	5.67	18.17	1.56	2.81
MEL-1B-4 PHI	24413	386.9	943	229941	44.2	49.7	266.2	1479
MEL-1B-5 PHI	1.56	1.12	1.46	1.16	2.82	2.40	1.17	1.03
MEL-1B>5 PHI	2.61	1.60	25.43	1.83	5.39	18.09	1.50	3.37
MEL-1C-4 PHI	28978	393.4	1151	232243	49.4	59.9	301.9	1596
MEL-1C-5 PHI	1.36	1.24	1.27	1.17	2.73	2.65	1.02	1.03
MEL-1C>5 PHI	2.31	1.65	21.70	1.83	5.06	14.80	1.37	3.59
MEL-1D-4 PHI	28032	411.7	1397	239462	57.4	72.7	329.6	1677
MEL-1D-5 PHI	1.50	1.23	1.18	1.16	2.47	2.43	1.04	1.04
MEL-1D>5 PHI	2.43	1.70	20.43	1.84	4.66	13.40	1.31	4.43
MEL-3A-4 PHI	23896	377.0	854	223404	40.2	45.3	256.9	1443
MEL-3A-5 PHI	1.46	1.06	1.52	1.16	3.05	2.53	1.13	1.04
MEL-3A>5 PHI	2.51	1.49	26.69	1.81	5.72	19.01	1.52	2.84
MEL-3B-4 PHI	24672	386.5	979	230060	43.7	52.6	270.4	1506
MEL-3B-5 PHI	1.56	1.13	1.43	1.17	2.95	2.35	1.09	1.03
MEL-3B>5 PHI	2.60	1.60	24.79	1.82	5.58	16.95	1.36	3.44
MEL-3C-4 PHI	25937	390.6	1223	238855	51.6	63.2	303.6	1614
MEL-3C-5 PHI	1.49	1.26	1.24	1.16	2.68	2.45	1.06	1.03
MEL-3C>5 PHI	2.57	1.66	21.57	1.83	4.82	14.88	1.36	3.91
MEL-3D-4 PHI	29917	419.9	1404	246896	59.2	76.6	328.4	1713
MEL-3D-5 PHI	1.43	1.23	1.20	1.13	2.44	2.39	1.06	1.04
MEL-3D>5 PHI	2.59	1.76	20.63	1.82	4.60	12.76	1.36	4.75
MEL-5A-4 PHI	24012	387.3	907	227669	41.9	47.8	261.7	1451
MEL-5A-5 PHI	1.51	1.05	1.50	1.16	2.85	2.30	1.15	1.03
MEL-5A>5 PHI	2.56	1.54	26.01	1.82	5.57	18.10	1.52	2.97
MEL-5B-4 PHI	25381	388.1	1091	231492	46.6	56.5	287.7	1537
MEL-5B-5 PHI	1.53	1.10	1.31	1.16	2.78	2.43	1.05	1.03
MEL-5B>5 PHI	2.57	1.62	22.82	1.82	5.26	16.11	1.42	3.52
MEL-5C-4 PHI	27668	397.7	1310	237075	53.3	67.4	309.2	1649
MEL-5C-5 PHI	1.42	1.23	1.19	1.16	2.60	2.52	1.06	1.03
MEL-5C>5 PHI	2.42	1.71	21.04	1.84	4.91	14.03	1.33	4.18
MEL-5D-4 PHI	37076	437.7	1483	280161	63.5	77.4	335.7	1775
MEL-5D-5 PHI	1.39	1.19	1.19	1.03	2.27	2.51	1.05	1.04
MEL-5D>5 PHI	2.46	1.71	19.95	1.61	4.78	13.29	1.42	4.73

phi group concentrations were generated. Noticeable differences between the concentrations of each of the phi groups exist. The 5 phi group concentrations for both beaches were 1.01 to 3.05 times greater than those of the 4 phi group while the > 5 phi group concentrations for both beaches were 1.31 to 27.41 times greater than those of the 4 phi group. Evidently, the 5 and > 5 phi groups contain significantly higher concentrations of heavy metals than that of the 4 phi group. Moreover, the > 5 phi group concentrations are significantly higher than that of the 5 phi group.

The above assessments of both the grain-size data and the heavy metal concentration data provide reasonable explanations for the restrictive grain-size fraction's inability to circumvent the effects of grain-size on the distribution of heavy metals. This is not to suggest, however, that the use of restrictive grain-size fractions do no effectively abate the effects of grain-size in all types of studies. It does, however, suggest that extreme caution must be taken when using a restrictive grain-size fraction to eliminate the effects of grain-size on the distribution of heavy metals. Several investigators including Axtman *et al.* (1997), Ntekim *et al.* (1993), Fatimad *et al.* (1988), Rule (1986) and Salomons and Forstner (1984) among others, have utilized the > 4 phi sediment fraction to minimize the grain-size dependencies of heavy metals. This investigation reveals that the use of a single sieve to generate a sediment population that is > 4 phi may result in the derivation of two totally different sample sets. Additional scrutiny of any restrictive grain-size fraction should always be conducted to ensure that the restrictive grain-size fraction has adequately minimized the effects of grain-size bias.

To suggest that the grain-size of sediment is the only variable that controls or influences the distribution of heavy metals would be erroneous. A multitude of variables have been implicated in influencing the spatial distribution of heavy metals including among others the source of the metals themselves, geochemistry (other metals and minerals), grain density, depth, pH, salinity, temperature and total organic content. True comparisons of the heavy metal concentrations of two or more beaches in different locations would require an assessment of all of the variables mentioned above. Such investigations have yet to be conducted. A totally encompassing investigation as this, would be extremely time consuming as well as costly, if at all possible. Many of the variables that influence the spatial distribution of heavy metals are interrelated themselves. For this reason, the majority of investigators that have sought to account for spatial variations in the concentrations of heavy metals focused on one or two of the controlling variables.

The two variables that have received the most attention are grain-size and geochemistry. Studies that have focused on grain-size only include among others those conducted by De Gregori *et al.* (1996), Mantei and Sappington (1994), Maurer *et al.* (1994), Chakrapani and Subramanian (1993), Grant and Middleton (1990), Fatimad et. al. (1988) and Sakai *et al.* (1986). Paulsen and Owen (1996), Leoni and Sartori (1997), Shine *et al.* (1995),McMurtry *et al.* (1995),Huang *et al.* (1994),Nair and Blanchard (1993) and Robbe *et al.* (1995) have all conducted studies that have focused solely on geochemistry as the primary controlling variable in the spatial distribution of heavy metals. Some investigators have attempted to integrate the effects of both grain-size and geochemistry. These investigations, however, are more general in nature, place a significant amount of emphasis on one of the two variables and lack statistical support.

Energy inputs into a coastal system determine whether a beach is accreting, stable or eroding. The primary difference between an accreting beach and an eroding beach in the same coastal system is the difference in the grain-size of sediments present within them. Since grain-size is the primary difference between the two beach types and the differences between the two beaches in this investigation are so pronounced an assessment of the heavy metal differences based on the variable grain-size was necessary. Moreover, by focusing on the effects of grain-size, the investigation was able to demonstrate the inability of the use of a restrictive grain-size fraction to circumvent the effects of grain-size bias.

CHAPTER 6

6.1 Conclusions and Recommendations:

The results of this investigation revealed that accreting beaches, with smaller grain-sizes and eroding beaches, with coarser grain-sizes exhibit contrasting concentrations of heavy metals. This was shown with the use of discriminant analysis. Albion beach, an accreting beach, contained higher concentrations of heavy metals than did Melanie beach, an eroding beach. The premise that variations in the concentrations of heavy metals between the two beach types was attributable to the grain-size of sediment was verified by the results of correlation and regression analysis. The results of the correlation and regression analysis revealed that an inverse relationship between heavy metal concentrations and the grain-size of sediment exists.

From the results of this investigation, it was also discovered that spatial variations in the concentrations of heavy metals are discernible and distinct in both across-shore and along-shore directions (westward) within accreting and eroding beaches. More specifically, heavy metal concentrations increased in a shoreward direction within Albion beach while increasing in a seaward direction within Melanie beach. Heavy metal concentrations also showed a tendency to increase in an east to west direction within both Albion and Melanie beach. The direction of heavy metal increase in across-shore and along-shore directions (westward) mimicked patterns of grain-size decrease within both beaches.

In addition to verifying both of the hypotheses forwarded in this investigation, questions surrounding the ability of restrictive grain-size fractions in reducing grain-size bas were raised. Although a restrictive grain-size fraction was used, significant effects of grain-size bias were discovered when correlation and regression analysis was performed. The need to scrutinize the granular composition of the restrictive grain-size fraction to ensure that its use has adequately minimized the effects of grain-size bias has been made clear.

Despite having concluded that the concentrations of heavy metals varies significantly between accreting and eroding beaches as well as within both beach types, additional investigations focusing on the role of grain-size in producing the results attained in this investigation should be conducted. Moreover, the scope of future investigations should be expanded to determine if the results are reproducible among other accreting and eroding regions along the Guyana coast and elsewhere. As well, the mineralogical properties of the sediments under investigation should also be investigated. In addition, chemical interactions among different metal types should also be examined.

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APPENDIX

Appendix Table 1: Grain-size Distribution (100g Sample)

ALBION SEDIMENT SAMPLES										
	2.0 (PHI)	2.2 (PHI)	2.4 (PHI)	2.6 (PHI)	2.8 (PHI)	3.0 (PHI)	3.5 (PHI)	4.0 (PHI)	5.0 (PHI)	>5.0 (PHI)
AL 1A	0.68	1.49	2.55	3.27	5.01	7.49	11.76	16.54	21.50	29.71
Al 1B	0.74	1.58	2.64	3.42	5.11	7.63	11.71	16.42	21.35	29.40
AL-1C	0.79	1.56	2.77	3.71	5.09	7.98	11.72	16.12	21.23	29.03
AL-1D	0.86	1.60	3.04	4.26	5.37	8.12	11.54	15.81	20.67	28.73
AL-3A	0.59	0.87	2.05	3.17	4.97	7.51	11.81	16.88	22.18	29.97
AL-3B	0.66	0.98	2.14	3.21	5.17	7.61	11.63	16.75	21.99	29.86
AL-3C	0.69	1.03	2.22	3.15	5.03	7.79	11.79	16.74	21.86	29.70
AL-3D	0.75	1.02	2.41	3.60	5.06	8.04	11.67	16.44	21.39	29.62
AL-5A	0.41	0.62	1.92	3.01	4.63	7.74	12.31	16.94	22.19	30.23
AL-5B	0.46	0.67	2.01	3.09	4.79	7.69	12.28	16.84	22.01	30.16
AL-5C	0.58	0.77	2.12	3.04	4.88	7.71	12.20	16.75	21.91	30.04
AL-5D	0.69	0.84	2.19	3.14	4.93	7.82	11.91	16.79	21.83	29.86
MELANIE SEDIMENT SAMPLES										
	2.0 (PHI)	2.2 (PHI)	2.4 (PHI)	2.6 (PHI)	2.8 (PHI)	3.0 (PHI)	3.5 (PHI)	4.0 (PHI)	5.0 (PHI)	>5.0 (PHI)
MEL-1A	16.91	15.42	13.02	8.98	6.25	7.97	7.55	7.66	9.67	6.57
MEL-1B	16.85	15.24	12.81	8.92	6.19	8.06	7.62	7.74	9.81	6.76
MEL-1C	16.64	15.20	12.93	8.86	6.14	8.01	7.73	7.80	9.88	6.81
MEL-1D	16.58	15.11	12.86	8.72	6.18	8.06	7.70	7.86	10.02	6.91
MEL-3A	16.86	15.19	13.03	9.00	6.20	7.99	7.56	7.71	9.74	6.72
MEL-3B	16.76	15.12	12.91	8.93	6.24	7.94	7.62	7.78	9.89	6.81
MEL-3C	16.63	15.05	12.87	8.80	6.25	8.01	7.64	7.82	10.03	6.90
MEL-3D	16.57	14.97	12.75	8.68	6.17	8.10	7.72	7.88	10.07	7.09
MEL-5A	16.61	15.04	12.89	8.89	6.22	8.11	7.60	7.79	10.06	6.79
MEL-5B	16.71	15.10	12.83	8.82	6.17	8.10	7.47	7.95	9.98	6.87
MEL-5C	16.57	14.91	12.85	8.65	6.19	8.04	7.60	8.01	10.05	7.13
MEL-5D	16.51	14.91	12.79	8.64	6.12	8.10	7.69	7.98	10.09	7.17

Appendix Table 2: Heavy Metal Concentrations for the > 4 Phi Bulk Sediment Samples (PPB)

	Al	Cr	Cu	Fe	Ni	Pb	V	Zn
ALBION BEACH								
AL 1A	188808	643.3	23546	390906	220.0	409.1	460.8	5996
Al 1B	164365	608.4	18619	356658	201.3	367.7	396.6	5362
AL-1C	125750	584.7	12796	342685	185.6	326.4	383.4	4054
AL-1D	123335	507.4	10702	329691	151.8	259.5	347.6	3258
AL-3A	202759	672.6	25394	408469	223.5	522.6	472.1	7758
AL-3B	169399	618.2	20625	368653	202.5	382.2	434.1	5628
AL-3C	136928	596.3	14589	345676	186.4	339.9	385.0	4479
AL-3D	125041	530.9	10601	335558	151.8	275.6	352.2	3772
AL-5A	210725	705.5	25129	425933	250.5	529.0	479.4	8504
AL-5B	173761	641.9	21894	370614	208.0	388.0	454.3	6294
AL-5C	144150	601.3	16800	356383	197.9	365.6	388.9	5192
AL-5D	125730	577.1	10788	337090	163.5	279.4	362.3	4013
MELANIE BEACH								
	Al	**Cr**	**Cu**	**Fe**	**Ni**	**Pb**	**V**	**Zn**
MEL-1A	37110	411.5	5032	251833	79.5	191.5	277.0	1906
MEL-1B	44136	414.2	6067	282609	85.6	217.1	296.3	2164
MEL-1C	46728	431.8	7187	285926	88.1	255.1	336.3	2518
MEL-1D	49022	510.2	9357	309998	95.6	274.5	388.8	2994
MEL-3A	40869	405.2	5066	265100	83.9	214.0	284.5	1920
MEL-3B	44978	418.1	6343	283233	86.6	228.2	298.3	2185
MEL-3C	46435	430.7	7886	302955	88.3	260.4	337.1	2609
MEL-3D	49506	512.8	9678	313022	97.6	325.9	391.4	3226
MEL-5A	42832	411.5	5587	28152	85.2	216.2	295.6	1958
MEL-5B	46068	428.6	6999	284239	86.7	234.5	315.2	2293
MEL-5C	47512	442.9	8211	300401	93.5	263.6	348.7	2703
MEL-5D	60079	529.6	10817	325527	113.6	232.0	404.8	3685

Appendix Table 3: Heavy Metal Concentrations for the 4 Phi, 5 Phi and > 5 Phi Sediment Groups (Albion Beach)

	Al	Cr	Cu	Fe	Ni	Pb	V	Zn
AL-1A-4 PHI	156991	430.4	1420	247070	66.2	67.7	286.2	1637
AL-1A-5 PHI	168695	558.4	1770	284671	147.5	170.4	387.6	1721
AL-1A>5PHI	232856	692.3	28442	454479	303.2	949.5	507.4	7274
AL-1B-4 PHI	119121	412.2	1205	240627	53.8	51.7	279.5	1640
AL-IB-5 PHI	142912	492.1	1618	267390	131.8	142.5	384.3	1657
AL-1B>5 PHI	202616	663.8	26211	430062	271.8	901.3	431.6	6508
AL-1C-4 PHI	91327	406.1	1021	234621	48.7	47.5	270.8	1571
AL-IC-5 PHI	117650	480.4	1409	257930	129.5	123.1	380.9	1603
AL-1C>5 PHI	183542	658.7	24796	418732	253	856.4	397.5	5702
AL-1D-4 PHI	86246	388.2	856	224063	41.6	41.4	272.4	1500
AL-ID-5 PHI	104379	441.7	1289	248492	125.4	97.6	367	1535
AL-1D>5 PHI	167943	550.3	23463	410470	249.7	821.1	388	4141
AL-3A-4 PHI	158290	433.9	1507	256458	61.3	70.4	288.3	1727
AL-3A-5 PHI	169773	584.2	1791	289737	140.4	184.7	385.3	1756
AL-3A>5 PHI	244301	727.3	29663	449237	291.6	1020.6	509.7	8371
AL-3B-4 PHI	127631	419.3	1293	245377	49.9	56.8	283.7	1653
AL-3B-5 PHI	153370	501.4	1656	274129	133.4	157.3	381.6	1694
AL-3B>5 PHI	216071	670	27307	439271	266.4	921.2	483.4	6635
AL-3C-4 PHI	97663	408.4	1089	232294	48.1	49.3	290	1577
AL-3C-5 PHI	123482	490.1	1477	259905	128.6	129.6	383.7	1612
AL-3C>5 PHI	191498	660.2	25308	420037	253.7	871.3	409.1	5939
AL-3D-4 PHI	91304	393.7	897	228846	43.8	44.8	284.3	1527
AL-3D-5 PHI	109276	474.8	1303	251092	119.8	104.3	366.4	1577
AL-3D>5 PHI	169420	568	23230	414739	243.1	832.7	397.2	4336
AL-5A-4 PHI	162310	441	1487	260065	55.7	73.9	290.6	1794
AL-5A-5 PHI	177623	588.6	1805	294637	139.6	191.5	391.4	1887
AL-5A>5 PHI	264201	756.3	29667	462628	284.4	1031.4	517.7	9200
AL-5B-4 PHI	131440	423.6	1346	247642	50.5	60.2	288.1	1711
AL-5B-5 PHI	160557	507.6	1694	273294	130.7	162	382.4	1737
AL-5B>5 PHI	226193	688.6	27996	442628	258.2	937.5	489.6	7108
AL-5C-4 PHI	99404	413.6	1155	238082	46.3	52.6	301.7	1608
AL-5C-5 PHI	137621	492.2	1520	263915	123.7	137.3	391.4	1650
AL-5C>5 PHI	197537	661.6	25940	428670	251.8	987.6	412.6	6212
AL-5D-4 PHI	88506	485.1	914	231479	41.5	43.1	291.1	1546
AL-5D-5 PHI	108871	477.5	1344	252721	121.6	117.7	385.8	1591
AL-5D>5 PHI	177617	621.3	23218	413940	243.7	827	403.5	5143

Appendix Table 4: Heavy Metal Concentrations for the 4 Phi, 5 Phi and > 5 Phi Sediment Groups (Melanie Beach)

	Al	Cr	Cu	Fe	Ni	Pb	V	Zn
MEL-1A-4 PHI	21632	388.7	818	218764	38.8	46.2	250.8	1405
MEL-1A-5 PHI	33914	402.6	1327	250632	119.7	112.7	277.4	1441
MEL-1A>5 PHI	57941	547.3	22414	394731	220.6	836.1	390.1	3946
MEL-1B-4 PHI	24413	386.9	943	229941	44.2	49.7	266.2	1479
MEL-1B-5 PHI	38128	432.7	1379	266750	124.7	119.9	297.6	1522
MEL-1B>5 PHI	63814	620.6	23816	419773	237.9	886.5	398.4	4990
MEL-1C-4 PHI	28978	393.4	1151	232243	49.4	59.9	301.9	1596
MEL-1C-5 PHI	38031	489.4	1472	271719	134.6	158.9	308.4	1639
MEL-1C>5 PHI	66881	650.2	25076	424760	248.1	887.7	412.3	5727
MEL-1D-4 PHI	28032	411.7	1397	239462	57.4	72.7	329.6	1677
MEL-1D-5 PHI	42066	506.5	1653	279671	141.4	176.6	340.8	1743
MEL-1D>5 PHI	68212	700.1	28516	442975	266.7	964.0	430.7	7425
MEL-3A-4 PHI	23896	377.0	854	223404	40.2	45.3	256.9	1443
MEL-3A-5 PHI	34817	400.1	1304	259314	121.7	114.6	291.0	1496
MEL-3A>5 PHI	60030	563.4	22701	402376	229.4	862.3	392.6	4102
MEL-3B-4 PHI	24672	386.5	979	230060	43.7	52.6	270.4	1506
MEL-3B-5 PHI	38543	437.7	1402	269423	127.6	123.7	294.3	1557
MEL-3B>5 PHI	64207	619.4	24217	420065	240.4	891.5	402.0	5175
MEL-3C-4 PHI	25937	390.6	1223	238855	51.6	63.2	303.6	1614
MEL-3C-5 PHI	38897	491.7	1512	277562	137.3	155.3	320.8	1663
MEL-3C>5 PHI	66812	647.9	26317	437201	251.6	937.1	413.7	6304
MEL-3D-4 PHI	29917	419.9	1404	246896	59.2	76.6	328.4	1713
MEL-3D-5 PHI	42875	518.3	1679	280743	144.3	183.7	350.6	1789
MEL-3D>5 PHI	71737	740.3	28940	448631	273.1	977.4	447.7	8136
MEL-5A-4 PHI	24012	387.3	907	227669	41.9	47.8	261.7	1451
MEL-5A-5 PHI	36215	404.7	1356	264851	120.0	110.3	291.3	1495
MEL-5A>5 PHI	61463	599.4	23563	416047	233.5	871.9	398.1	4304
MEL-5B-4 PHI	25381	388.1	1091	231492	46.6	56.5	287.7	1537
MEL-5B-5 PHI	38790	427.4	1433	270045	129.4	136.4	303.4	1579
MEL-5B>5 PHI	65319	630.2	24885	421379	242.7	902.6	409.7	5408
MEL-5C-4 PHI	27668	397.7	1310	237075	53.3	67.4	309.2	1649
MEL-5C-5 PHI	39212	490.1	1560	275631	137.9	170.2	327.8	1702
MEL-5C>5 PHI	66937	680.3	27334	436450	260.2	940.2	412.2	6891
MEL-5D-4 PHI	37076	437.7	1483	280161	63.5	77.4	335.7	1775
MEL-5D-5 PHI	51664	521.6	1770	288632	143.2	195.4	351.3	1845
MEL-5D>5 PHI	91271	748.7	29494	450238	301.4	1023.7	477.0	8726

Appendix Table 5: Across-Shore Deviations in Heavy Metal Concentrations (>4 Phi Samples)

	Al	Cr	Cu	Fe	Ni	Pb	V	Z
ALBION 1A	188808	643.3	23546	390906	250.5	409.1	460.8	5996
ALBION 1B	164365	608.4	18619	356658	208	367.7	396.6	5362
ALBION 1C	125750	584.7	12796	342685	197.9	326.4	383.4	4054
ALBION 1D	123335	507.4	10702	329691	163.5	259.5	347.6	3258
ALBION 3A	**202759**	**672.6**	**25394**	**408469**	**223.5**	**522.6**	**472.1**	**7758**
ALBION 3B	**169399**	**618.2**	**20625**	**368653**	**202.5**	**382.2**	**434.1**	**5628**
ALBION 3C	**136928**	**596.3**	**14589**	**345676**	**186.4**	**339.9**	**385.0**	**4479**
ALBION 3D	**125041**	**530.9**	**10601**	**335558**	**151.8**	**275.6**	**352.2**	**3772**
ALBION 5A	210725	705.5	25129	425933	220	529.0	479.4	8504
ALBION 5B	173761	641.9	21894	370614	201.3	388.0	454.3	6294
ALBION 5C	144150	601.3	16800	356383	185.6	365.6	388.9	5192
ALBION 5D	125730	577.1	10788	337090	151.8	279.4	362.3	4013
MELANIE 1A	37110	411.5	5032	251833	79.5	191.5	277.0	1906
MELANIE1B	44136	414.2	6067	282609	85.6	217.1	296.3	2164
MELANIE IC	46728	431.8	7187	285926	88.1	255.1	336.3	2518
MELANIE ID	49022	510.2	9357	309998	95.6	274.5	388.8	2994
MELANIE 3A	**40869**	**405.2**	**5066**	**265100**	**83.9**	**214.0**	**284.5**	**1920**
MELANIE 3B	**44978**	**418.1**	**6343**	**283233**	**86.6**	**228.2**	**298.3**	**2185**
MELANIE 3C	**46435**	**430.7**	**7886**	**302955**	**88.3**	**260.4**	**337.1**	**2609**
MELANIE 3D	**49506**	**512.8**	**9678**	**313022**	**97.6**	**325.9**	**391.4**	**3226**
MELANIE 5A	42832	411.5	5587	28152	85.2	216.2	295.6	1958
MELANIE 5B	46068	428.6	6999	284239	86.7	234.5	315.2	2293
MELANIE 5C	47512	442.9	8211	300401	93.5	263.6	348.7	2703
MELANIE 5D	60079	529.6	10817	325527	113.6	232.0	404.8	3685

Note: Arrow denotes direction of heavy metal concentration increase

Appendix Table 6: Along-Shore Deviations in Heavy Metal Concentrations (>4 Phi Samples)

	Al	Cr	Cu	Fe	Ni	Pb	V	Z
ALBION 1A	188808	643.3	23546	390906	220.0	409.1	460.8	5996
ALBION 3A	202759	672.6	25394	408469	223.5	522.6	472.1	7758
ALBION 5A	210725	705.5	25129	425933	250.5	529.0	479.4	8504
ALBION 1B	**164365**	**608.4**	**18619**	**356658**	**201.3**	**367.7**	**396.6**	**5362**
ALBION 3B	**169399**	**618.2**	**20625**	**368653**	**202.5**	**382.2**	**434.1**	**5628**
ALBION 5B	**173761**	**641.9**	**21894**	**370614**	**208.0**	**388.0**	**454.3**	**6294**
ALBION 1C	125750	584.7	12796	342685	185.6	326.4	383.4	4054
ALBION 3C	136928	596.3	14589	345676	185.4	339.9	385.0	4479
ALBION 5C	14415	601.3	16800	356383	197.9	365.6	388.9	5192
ALBION 1D	**123335**	**507.4**	**10702**	**329691**	**151.8**	**259.5**	**347.6**	**3258**
ALBION 3D	**125041**	**530.9**	**10601**	**335558**	**163.5**	**275.6**	**352.2**	**3772**
ALBION 5D	**125730**	**577.1**	**10788**	**337090**	**151.8**	**279.4**	**362.3**	**4013**
MELANIE 1A	37110	411.5	5032	251833	79.5	191.5	277.0	1906
MELANIE 3A	40869	405.2	5066	265100	83.9	214.0	284.5	1920
MELANIE 5A	42832	411.9	5587	28152	85.2	216.2	295.6	1958
MELANIE IB	**44136**	**414.2**	**6067**	**282609**	**85.6**	**217.1**	**296.3**	**2164**
MELANIE 3B	**44978**	**418.1**	**6343**	**283233**	**83.6**	**228.2**	**298.3**	**2185**
MELANIE 5B	**46068**	**428.6**	**6999**	**284239**	**86.7**	**234.5**	**315.2**	**2293**
MELANIE 1C	46728	431.8	7187	285926	88.3	255.1	336.3	2518
MELANIE 3C	46435	430.7	7886	302955	88.1	260.4	337.1	2609
MELANIE 5C	47512	442.9	8211	300401	93.5	263.6	348.7	2703
MELANIE 1D	**49022**	**510.2**	**9357**	**309998**	**95.6**	**274.5**	**388.8**	**2994**
MELANIE 3D	**49506**	**512.8**	**9678**	**313022**	**97.6**	**325.9**	**391.4**	**3226**
MELANIE 5D	**60079**	**529.6**	**10817**	**325527**	**113.6**	**232.0**	**404.8**	**3685**

Note: Arrow denotes
direction of heavy metal
concentration increase

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